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Measurement of degree of dispersion of pigments in water-based flexographic inks using color strength of prints.

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MEASUREMENT OF DEGREE OF DISPERSION OF PIGMENTS IN WATER-BASED FLEXOGRAPHIC INKS USING COLOR STRENGTH OF PRINTS

by

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CERTIFICATE OF APPROVAL

This thesis is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science

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ABSTRACT

The color strength method proposed by Nippert has been studied for the assessment of the pigment dispersion in water-based flexographic inks.

The assumptions of this new method are: (i) all of the ink penetrates the porous paper substrate to form a single uniform layer; (ii) the paper substrate replaces the white ink in the conventional color determination, so that the ink need not be diluted with an opaque white ink. Nippert derived the equation:

$$K/S = (k/S_p) \cdot c \ , \qquad (1)$$

where K/S is the ratio of the Kubelka-Munk absorption and scattering coefficients of the prints, k the absorption coefficient of the pigment, S_p the scattering coefficient of the paper, and c the weight of the ink film per unit area of paper. Thus a plot of K/S versus c should give a straight line through the origin, the slope of which (k/S_p) should be a measure of the degree of dispersion.

The term c in Equation (1) was re-defined in the present work as the weight of the pigment printed per unit area of paper, which expresses Equation (1) more correctly because K/S is a function of the optical properties of pigment and paper.

It was found that the choice of paper substrate

affected the linearity of the ($\underline{K}/\underline{S}$)-$\underline{c}$ plots. With a smooth-surfaced coated paper (Mead Offset), the color strength did not vary with pigment weight as predicted. For a porous synthetic polyolefin paper (duPont Tyvek), the ($\underline{K}/\underline{S}$)-$\underline{c}$ plots were linear up to 0.1 g/m^2 pigment weight, and the slopes of the straight lines increased with increasing milling time; above 0.1 g/m^2, the curves flattened out because the paper was saturated with ink. For a lighter coated paper (Finch Offset), the ($\underline{K}/\underline{S}$)-$\underline{c}$ plots were not linear, but instead were sigmoidal; this variation was attributed to the rougher surface of this paper. In general, the color strengths of the prints varied characteristically for different pigments. Moreover, for prints of comparable pigment weights, the color strengths increased with the milling time.

It was also demonstrated that the new method can distinguish the difference between the dispersing power of various resins.

Thus, this new color strength method gives nearly the same results as conventional color measurements for uncoated and lightly coated papers and offers promise as a routine measurement for the degree of dispersion.

INTRODUCTION

Dry powdered pigment usually comprises aggregates of primary particles which may be attached to other aggregates or primary particles forming agglomerates[1]. The size of the primary particles in most powdered pigments is usually well below 1 μm. With many organic pigments and most carbon blacks, the primary particle size is below 0.1 μm. On the other hand, in most powdered pigments, the agglomerates are 30-100 μm in size; otherwise the pigments would not be a powder, but would be in the form of a dust or smoke and could not be handled[2].

In use, the pigment is incorporated into a suitable vehicle and the system is ground or milled or dispersed in order to break down these aggregates and agglomerates until their sizes are in the submicron region. As the dispersion proceeds, the technological properties of the system change. On the other hand, the dispersion process is costly in terms of time required and mechanical energy expended. Thus, the control of the dispersion process is important for quality control and elimination of unnecessary cost.

Control requires the measurement of the dispersion state. The degree of dispersion of a printing ink can be determined by various methods as reviewed in detail else-

where[2,3]: electron microscopy or ultra-centrifugation as definitive methods which are not easily adapted to routine industrical practice; gloss measurements of printing ink films; sieve analysis of diluted inks; fineness-of-grind measurements using the NPIRI Production Grindometer; or color strength as a routine industrical method. Sieve analysis, print gloss, and fineness of grind detect only the largest particles in the dispersion, while color strength gives an indirect measure of the mean particle size. Hence, the color strength method has been studied further in this work.

Color strength is defined broadly as the ability of a colored material, such as an ink, to impart its color to a particular white medium. Measurement of color strength is usually carried out by a tinting method[2,4] based on the Kubelka-Munk theory. Color strength determined in this way is sometimes called tinting or tinctorial strength. Although this method is quite accurate, it is time-consuming. Furthermore, most ink makers prepare proof prints to test both the printability and final appearance of their products. Therefore, it is desirable to determine the relationship between an ink's tinting strength and its final appearance on a print, so that both tests can be combined into one.

Zorll attempted to develop such a method[5]. He

investigated the change in reflectance at increasing print weights for dispersions. Although he found a correlation between tinting strength and color strength of a proof print, his empirical work did not explain his results using color theory. Recently, Nippert has developed a new, simple color strength method[6] which he named "printing strength method" to distinguish from the conventional one. The applicability of his new method has been demonstrated for phthalocyanine blue dispersion in organic solvent-based vehicles.

The work described in this report extends Nippert's method for organic solvent-based inks to water-based flexographic inks. First, the influence of the paper on Nippert's method has been studied, because the paper plays a critical role in his method. Second, Nippert's method has been applied to the pigment dispersion in different resins to show the different dispersing powers of these resins.

All experiments have been carried out on the basis of the change in color strength of the pigment versus the milling time.

COLOR STRENGTH METHODS

It has long been known that, as grinding proceeds, color strength will increase. For many pigments the increase in color strength can be considerable. Color strength can be compared very accurately by the human eye and can also be measured by instruments, such as spectrophotometers. Color strength would, therefore, appear to provide a suitable means for measuring changes in pigment dispersion. The ink film with the higher color strength contains the more highly dispersed pigment.

A. The Kubelka-Munk Theory; Tinting Strength

The most general color strength method is based on the Kubelka-Munk theory. Kubelka and Munk set up and solved the basic differential equations and showed how the algebraic solution to these equations can be used to determine the reflectance of a colored film[7-9].

This theory is based on the assumption that a turbid film, not necessary opaque, can be considered homogeneous. Furthermore, it is assumed that the light entering the film is perfectly diffused. These assumptions make it possible to assume that the light goes either up or down within the film, that is, the light travels in only two channels: an upward channel and a downward channel.

The Kubelka-Munk theory also assumes that the light is either scattered in the opposite direction or absorbed as it passes through the film. Both the amounts of light scattered and absorbed from a given direction (upward or downward) are proportional to the amount in that direction. Based on these assumptions, Kubelka derived a system of differential equations which describes the flow density of light in both directions:

$$dj = -(S + K)j\,dx + Si\,dx \tag{2a}$$

$$-di = -(S + K)i\,dx + Sj\,dx\,, \tag{2b}$$

where K = the absorption coefficient of the film

S = the scattering coefficient of the film

i = the downward-proceeding light flux

j = the upward-proceeding light flux

dx = the thickness of elementary layer in the film

di = the total change of the downward-proceeding flux, i, during its passage through dx

dj = the total change of the upward-proceeding flux, j, during its passage through dx.

Solution of these equations gives the following expression:

$$R = \frac{1 - R_g[a - b\coth(bSX)]}{a - R_g + b\coth(bSX)}\,, \tag{3a}$$

where $a = 1 + K/S$ (3b)

$$b = (a^2 - 1)^{1/2} \tag{3c}$$

R = the reflectance of the film

X = the thickness of the film

R_g = the reflectance of the background over which the film lies.

When the film is opaque, that is, the film has such thickness that increasing the thickness would have no effect on the reflectance, the following algebraic expression can be obtained:

$$R_\infty = 1 + \left(\frac{K}{S}\right) - \left[\left(\frac{K}{S}\right)^2 + 2\left(\frac{K}{S}\right)\right]^{1/2} , \qquad (4a)$$

the inverse of this equation is

$$\frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} , \qquad (4b)$$

where R_∞ = the reflectance of the film at infinite thickness.

Therefore, if R_∞ is known, K/S can be calculated and vice versa.

There is the following useful relationship that both the absorption and the scattering coefficients can be built up from the individual absorption and scattering coefficients of pigments in the film:

$$\frac{K}{S} = \frac{c_1k_1 + c_2k_2 + \ldots + K_s}{c_1s_1 + c_2s_2 + \ldots + S_s} , \qquad (5)$$

where c = concentrations of pigments

k = unit absorption coefficients of pigments

s = unit scattering coefficients of pigments

subscripts 1, 2,... = the identifiers for the individual pigments in the film

K_s = the absorption coefficient of the substrate

S_s = the scattering coefficient of the substrate.

What has been described so far is the two-constant Kubelka-Munk theory, the two constants being the absorption coefficient and the scattering coefficient. In certain applications, a simplification of the theory known as single-constant theory can be used.

For pastel shades in paints or inks, by far the largest single constituent of the pigment mixture is titanium dioxide or some other high-scattering white pigment. Adding very small amounts of colored pigment hardly changes the scattering power of the film, which is largely due to the white pigment. The overall scattering coefficient can therefore be considered to be a constant, that is, the denominator in Equarion (5) is a constant. This means that the $\underline{K}/\underline{S}$ ratio can be built up in the following manner:

$$\frac{K}{S} = c_1\left(\frac{k}{s}\right)_1 + c_2\left(\frac{k}{s}\right)_2 + \ldots + \left(\frac{K}{S}\right)_s . \qquad (6)$$

The ratio $\underline{k}/\underline{s}$ is now a parameter on its own even though it is a ratio, and really amounts to only a single constant instead of the two.

If the film contains a large amount of titanium dioxide and only one very small amount of colored pigment, Equation (6) is reduced to

$$\frac{K}{S} = c\left(\frac{k}{s}\right) + \left(\frac{K}{S}\right)_s , \qquad (7)$$

where c = the concentration of single colored pigment

$(1-c)$ = the concentration of titanium dioxide

$(K/S)_s$ = the parameter due to titanium dioxide.

Equation (7) shows that, if the K/S value is plotted against the concentration of single colored pigment, a straight line should be obtained. The slope of this line is the unit k/s value required to characterize the color strength of the print.

B. Nippert's Method; Printing Strength

Nippert has developed an alternative technique to the general color strength method described above, that would allow the determination of a "printing strength" value from colorimetric analysis of proof prints without reducing the ink with an opaque white[6].

He called his model a single-layer model in which it is assumed that all of the ink penetrates the paper substrate to form a single uniform layer. Furthermore, he assumed that the absorption coefficient of the paper is small compared to that of the ink, while the scattering

coefficient of the paper is large compared to that of the ink; therefore, the paper substrate replaces the white ink in the tinting strength determination so that the ink need not be diluted with an opaque white ink.

If the ink contains only one colored pigment, the following equation can be obtained from Equation (5):

$$\frac{K}{S} = \frac{ck + K_p}{cs + S_p} , \qquad (8)$$

where K and S = the absorption and scattering coefficients of the proof prints

k and s = the unit absorption and scattering coefficients of the pigment

K_p and S_p = the absorption and scattering coefficients of the paper

c = the weight of the ink film per unit area of paper.

Since $\underline{S}_p$ is much larger than $\underline{cs}$, and $\underline{ck}$ is much larger than $\underline{K}_p$, Equation (8) could be approximated by

$$K/S = (k/S_p) \cdot c . \qquad (1)$$

This equation shows that a plot of $\underline{K}/\underline{S}$ versus $\underline{c}$ gives a straight line through the origin, the slope of which ($\underline{k}/\underline{S}_p$) should be a measure showing the state of the pigment dispersion.

EXPERIMENTAL DETAILS

Part I. Influence of paper

The influence of the paper on Nippert's method was investigated. The papers used were Finch Offset (lighter coated paper), duPont Tyvek (spunbonded olefin paper)[10], and Mead Offset (smooth-surfaced coated paper). Three different pigments, diarylide yellow, barium lithol red, and phthalocyanine blue, were used. Their commercial names are shown in Table 2. Joncryl 67 (styrene-acrylic resin, S. C. Johnson & Son, Inc.) was employed as a resin in all the experiments in this part.

Table 1 shows the formulation of the Joncryl 67 aqueous solution. The opaque white base was prepared for the measurements of tinting strength by milling the formulation shown in Table 2 with glass beads of diameter 3 mm on the Red Devil Paint Shaker for 1 hour. Table 2 also gives the formulations of yellow, red, and blue mill bases. In these mill bases, the pigment-to-solid resin weight ratio was held at 1 : 1.

The mill base 140 g and glass beads 95 g were put in a 8 ounce low glass bottle and milled for a total of 8 hours on the Red Devil Paint Shaker with samples of the pigment dispersion taken at 10 min, 30 min, 1 hr, 2 hr, 4 hr, 6 hr, and 8 hr.

Table 1

Formulation of Joncryl 67 Vehicle

	wt%
Joncryl 67	27.5
Ammonia (28%)	6.5
Water	66.0
	100.0
pH	8.4
Viscosity (25°C)	210 cps

Table 2

Ink Formulations with Joncyl 67 Vehicle

	White	Yellow	Red	Blue
	wt%	wt%	Wt%	wt%
Pigment*	45.0	14.0	15.0	15.0
Joncryl 67 Vehicle	36.4	56.0	56.0	60.0
Isopropyl Alcohol	10.0	10.0	10.0	10.0
Water	8.6	20.0	19.0	15.0
	100.0	100.0	100.0	100.0
Pigment : Resin	4.5:1.0	1.0:1.1	1.0:1.0	1.0:1.1
Viscosity**	-	22.2"	26.0"	23.1"

*Pigments: Titanium Dioxide R-760 (New Jersey Zinc)
Permanent Yellow GR11-1300 (American Hoechst)
Barium Lithol Red 20-4210 (American Cyanamid)
Cyan Blue XR55-3761 (American Cyanamid)

**Viscosity was measured by Zahn Cup #2 at 25°C after 8-hr milling.

For measurements of tinting strength, reductions of the pigment dispersion samples were made with the opaque white so that the weight ratios of the colored pigment to titanium dioxide were approximately 1:99, 2:98, 5:95, and 10:90. These reductions were drawn down on the smooth side of Finch Offset paper by #8 wire coating rod (R. D. Specialties).

On the other hand, for measurements of printing strength, the proof prints were prepared by printing the pigment dispersion samples directly on the rougher sides of Finch Offset and duPont Tyvek papers using Anilox hand-rollers (Pamarco Inc.). Mead Offset paper was used only for printing the yellow pigment dispersion of 8-hours milling. The weight of paper was measured before and after printing.

These print samples were analyzed by a KCS-40 spectrophotometer (Kollmorgen Corp.). Their color strengths were determined from spectral reflectance values, taken at the wavelength of maximum absorption.

Part II. Variation of Type of Resin

In order to investigate the ability of Nippert's method to determine the dispersion state of the pigment dispersion in the different resin systems, the following resins were examined and compared with the Joncryl 67

system: Joncryl 678 (S. C. Johnson & Son), and Cropolamid 18W26, 18W58, and 18W59 (Crosby Chemical). Diarylide yellow (Permanent Yellow GR11-1300, Americal Hoechst) was used as a test pigment.

Table 3 shows the formulations of aqueous solutions of these resins. The Joncryl 678 and Cropolamid 18W26 systems were employed for both measurements of tinting and printing strengths of diarylide yellow, while only tinting strength was measured in the Cropolamid 18W58 system and only printing strength of the Cropolamid 18W59 system was studied because of small amounts of these resins.

Tables 4 and 5 present the mill base formulations of diarylide yellow and titanium dioxide, respectively, dispersed in Joncryl 678, and Cropolamid 18W26 and 18W58 for measurements of tinting strength. The pigment-to-solid resin weight ratios in these mill bases were held at the same values as those in yellow and white bases of the Joncryl 67 system.

Table 6 gives the mill base formulations of diarylide yellow in Joncryl 678 and Cropolamid 18W26 and 18W59 for measurements of printing strength. As can be seen, the solid resin contents in the Cropolamid 18W26 and 18W59 systems are lower than that in the Joncryl 678 system, which has the same formulation as the Joncryl 67 system. It was assumed in Nippert's derivation that all of the ink

Table 3

Vehicle Formulations of Joncryl 678 and Cropolamid 18W26, 18W58, and 18W59

	Joncryl	Cropolamid		
	678	18W26	18W58	18W59
	wt%	wt%	wt%	wt%
Resin	27.5	25.0	22.0	25.0
Ammonia (28%)	6.5	3.0	3.5	3.0
Isopropyl Alc.	-	15.0	-	15.0
Water	66.0	57.0	74.5	57.0
	100.0	100.0	100.0	100.0
pH	8.5	8.0	8.1	8.0
Viscosity (25°C)	60cps	120cps	1200cps	800cps

Table 4

Mill Base Formulations of Diarylide Yellow in Joncryl 678 and Cropolamid 18W26 and 18W58 for Measurements of Tinting Strengths

	Joncryl	Cropolamid	
	678	18W26	18W58
	wt%	wt%	wt%
Diarylide Yellow	14.0	14.0	14.0
Resin Vehicle	56.0	61.6	70.0
Isopropyl Alc.	10.0	10.0	10.0
Water	20.0	14.4	6.0
	100.0	100.0	100.0
Pigment : Resin	1.0:1.1	1.0:1.1	1.0:1.1

Table 5

Mill Base Formulations of Titanium Dioxide in Joncryl 678 and Cropolamid 18W26 and 18W58 for Measurements of Tinting Strengths

	Joncryl 678	Cropolamid 18W26	Cropolamid 18W58
	wt%	wt%	wt%
Titanium Dioxide	45.0	45.0	45.0
Resin Vehicle	36.4	40.0	45.5
Isopropyl Alc.	10.0	10.0	5.0
Water	8.6	5.0	5.0
	100.0	100.0	100.0
Pigment : Resin	4.5:1.0	4.5:1.0	4.5:1.0

Table 6

Mill Base Formulations of Diarylide Yellow in Joncryl 678 and Cropolamid 18W26 and 18W59 for Measurements of Printing Strengths

	Joncryl 678	Cropolamid 18W26	Cropolamid 18W59
	wt%	wt%	wt%
Diarylide Yellow	14.0	14.0	14.0
Resin Vehicle	56.0	40.0	34.0
Isopropyl Alc.	10.0	30.0	32.0
Water	20.0	16.0	20.0
	100.0	100.0	100.0
Pigment : Resin	1.0:1.1	1.0:0.7	1.0:0.6
Viscosity*	21.5"	21.8"	24.0"

*Viscosity was measured by Zahn Cup #2 at 25°C after 8-hours milling.

penetrates the paper substrate to form a single uniform layer. To keep this assumption valid, all the inks of interest should have the same viscosity. The difference in formulations between the Joncryl 67 and 678 systems and the Cropolamid 18W26 and 18W59 systems is attributed to this point. As shown in Table 6, the viscosities of these inks were about 21-22 seconds/Zahn Cup #2 after 8-hours milling.

On the other hand, in the case of tinting strength, since the printing film contains a large amount of titanium dioxide and is opaque, the thickness of the film can be assumed to be infinite and its change does not affect the reflectance value of the film. Hence, the difference of viscosities between the inks of interest is not an important factor, and the pigment-to-solid resin ratio was set constant in all the mill bases.

These mill bases were ball-milled on the Red Devil Paint Shaker and samples were examined in the same way as described in Part I. Finch Offset paper was used in both experiments of tinting and printing strengths.

DISCUSSION OF RESULTS

Part I. Influence of Paper

A. Tinting Strength

The experimental data and results for tinting strength of diarylide yellow, barium lithol red, and phthalocyanine blue in Joncryl 67 are given in Appendices A-1, A-2, and A-3, respectively. The reflectance values were taken at the wavelength of maximum absorption, i.e., 440, 560, and 610 nm for yellow, red, and blue, respectively.

When the experimental reflectance value, R_m, was converted into the K/S value and plotted against the colored pigment concentration, a curve that was concave downward was obtained instead of a straight line. It is known that this phenomenon results from the refractive-index discontinuity between air and the film. Light striking the film is partially reflected at the boundary. Also, a certain amount of the light emerging from the film is reflected at the boundary back into the film. Saunderson treated this situation mathematically and derived an equation known as the Saunderson correction (11,12):

$$R_t = \frac{R_m - k_1}{1 - k_1 - k_2 + k_2 R_m} , \qquad (9)$$

where R_m = the experimental reflectance

R_t = the theoretical reflectance

k_1 = the front-surface reflectance of the film

k_2 = the internal reflectance of the film.

Thus, by Equation (9), $\underline{R}_t$ was calculated from $\underline{R}_m$ with $\underline{k}_1 = 0.035$ and $\underline{k}_2 = 0.6$. The $\underline{R}_t$ values were then converted into the $\underline{K}/\underline{S}$ by Equation (4b). The $\underline{K}/\underline{S}$ was plotted against the colored pigment concentration, $\underline{c}$. Figures 1, 2, and 3 show these results for diarylide yellow, barium lithol red, and phthalocyanine blue, respectively. According to Equation (7), the slope of the $(\underline{K}/\underline{S})$-$\underline{c}$ plot represents the $\underline{k}/\underline{s}$ of the colored pigment, that is, the tinting strength, and the intercept gives the $\underline{K}/\underline{S}$ of titanium dioxide, which is nearly equal to zero in the figures. The $\underline{K}/\underline{S}$ of titanium dioxide was obtained from the other experiment. The reflectance of the print of titanium dioxide dispersion in Joncryl 67 was measured and analyzed similarly. As shown in Appendix B, the $\underline{K}/\underline{S}$ of titanium dioxide in Joncryl 67 is of the order of magnitude of 10^{-3}.

The $\underline{k}/\underline{s}$ values of colored pigments were obtained graphically from Figures 1, 2, and 3, and plotted as a function of the milling time in Figure 4.

B. Printing Strength

The experimental data and results for printing

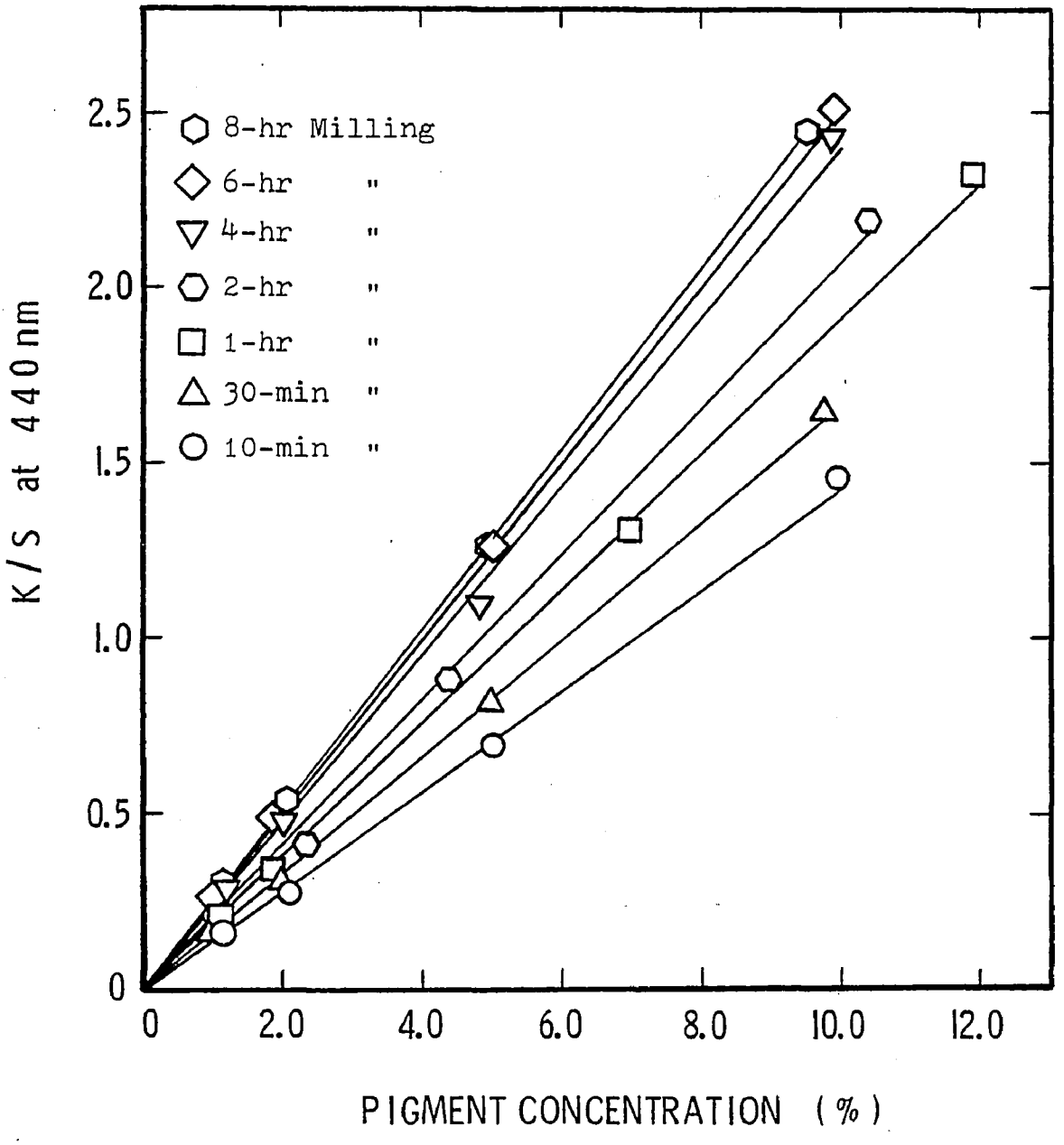

Figure 1 K/S versus Pigment Concentration Curves for Diarylide Yellow Dispersion in Joncryl 67, by Tinting Analysis

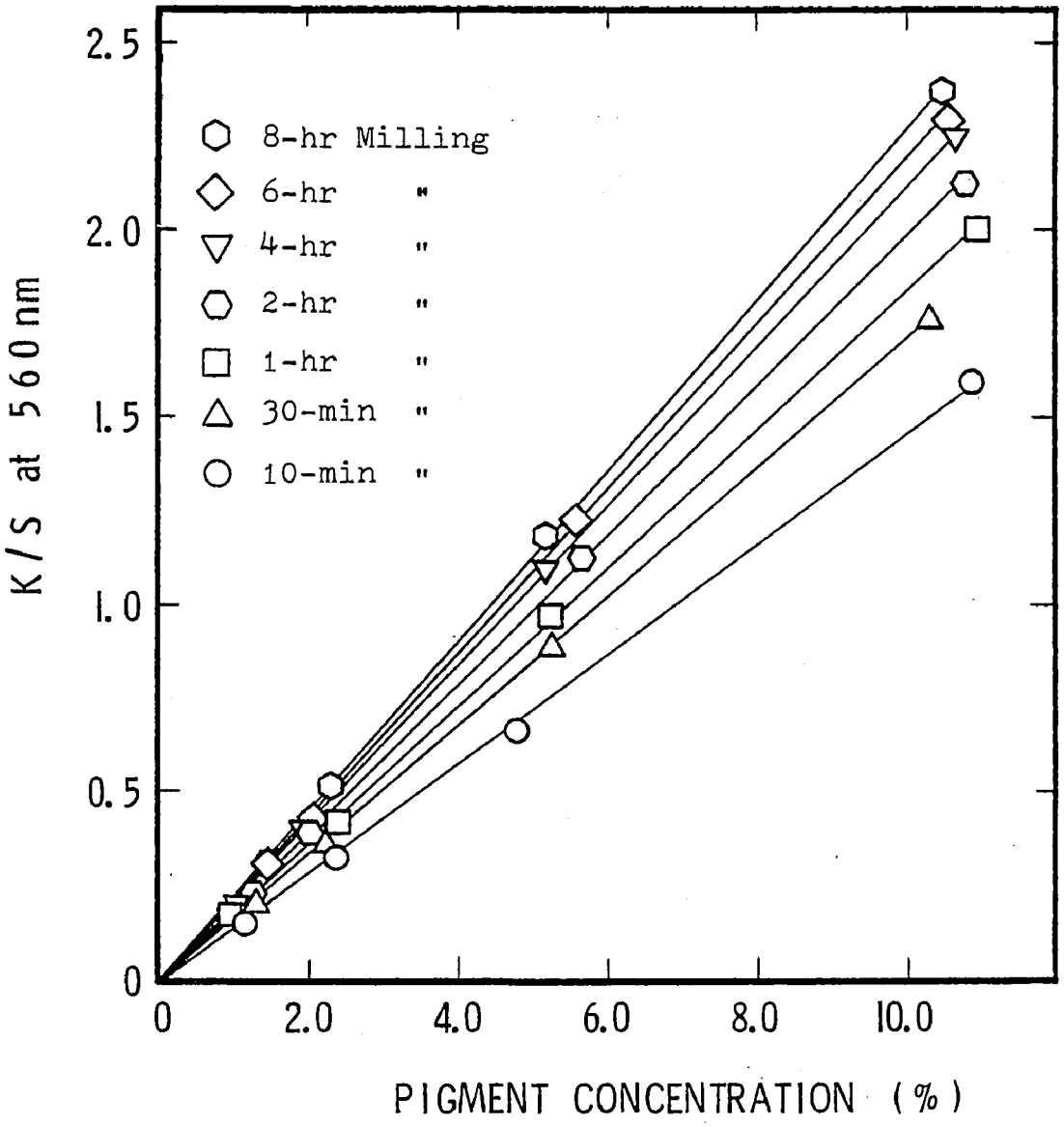

Figure 2 K/S versus Pigment Concentration Curves for Barium Lithol Red Dispersion in Joncryl 67, by Tinting Analysis

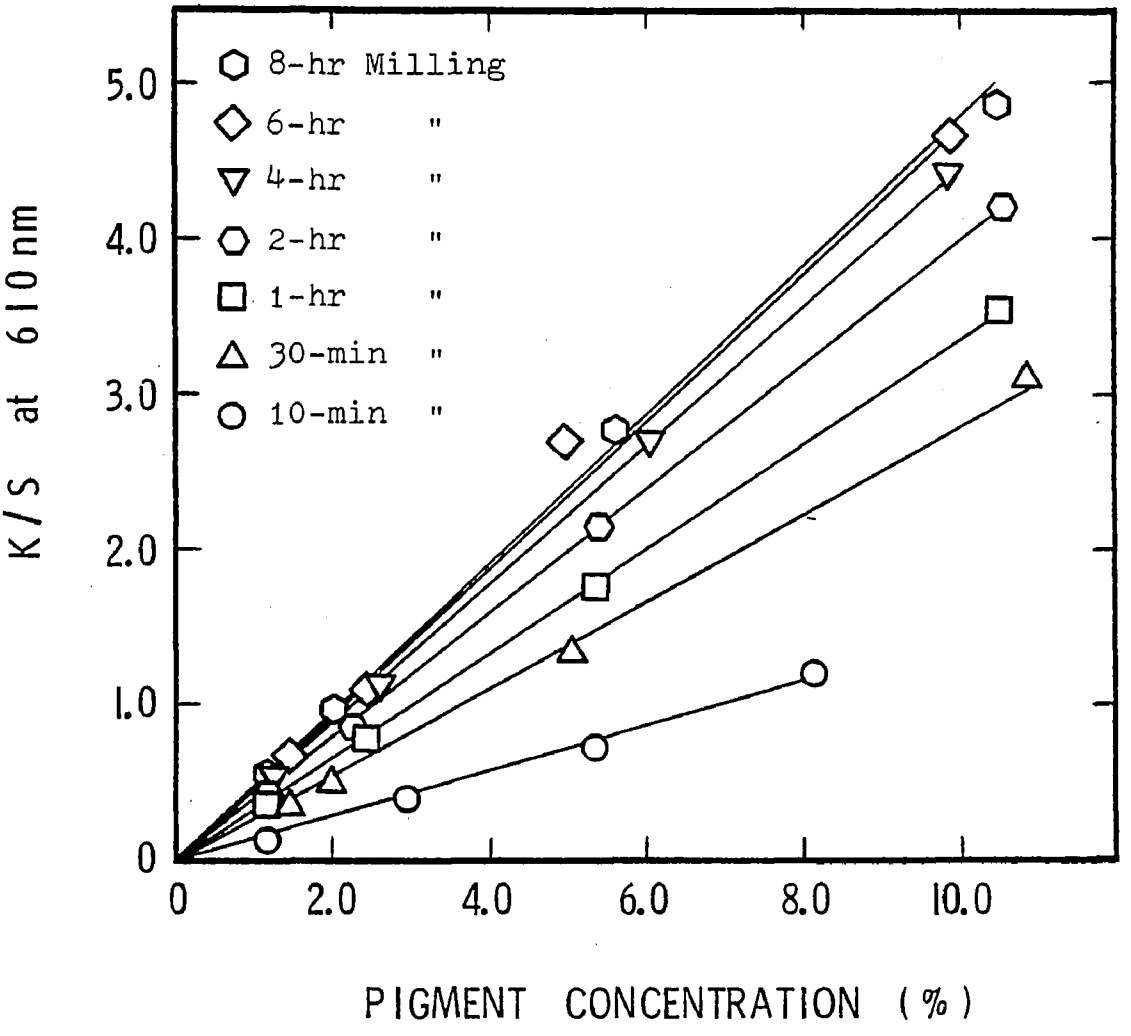

Figure 3 K/S versus Pigment Concentration Curves for Phthalocyanine Blue Dispersion in Joncryl 67, by Tinting Analysis

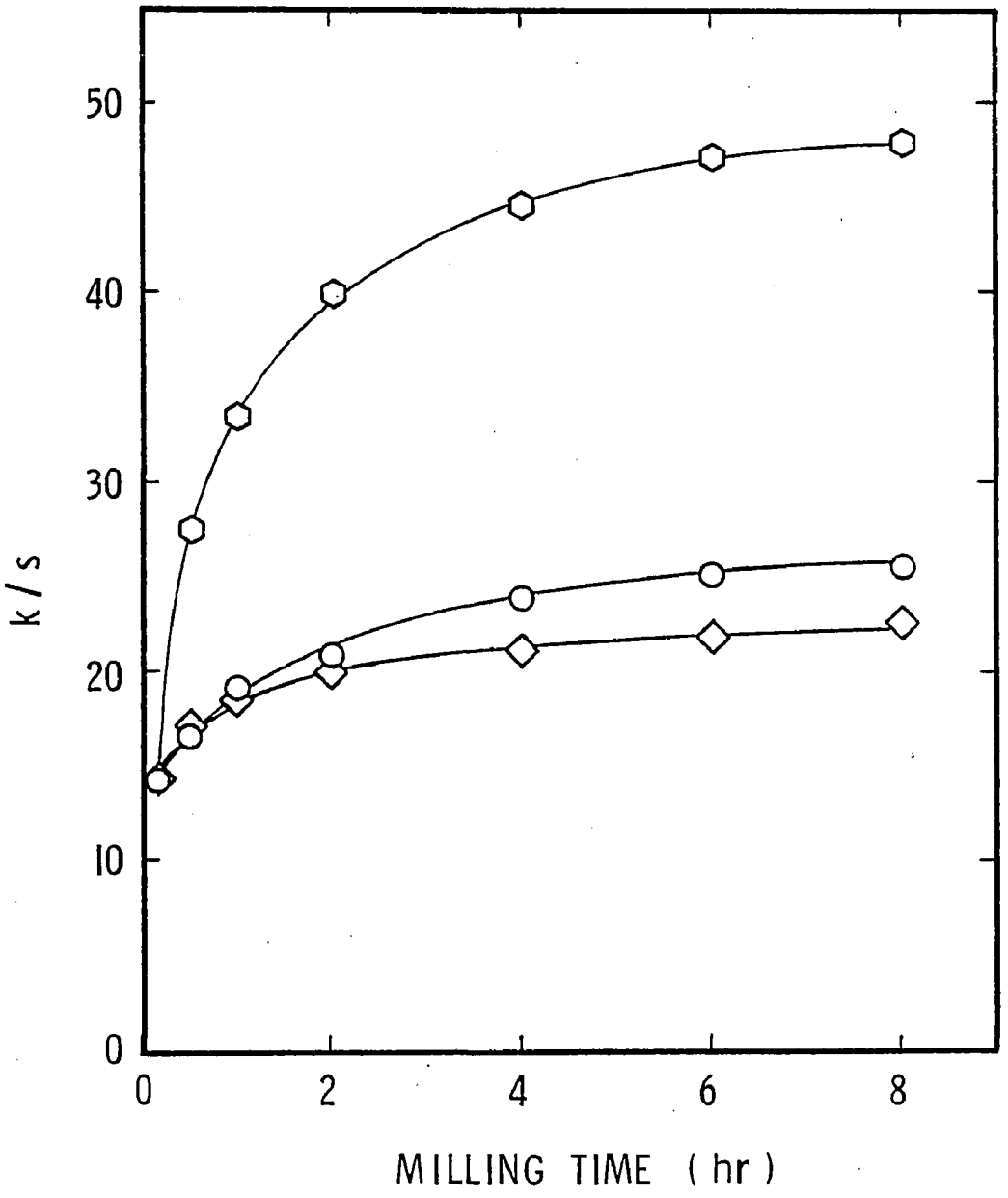

Figure 4 Tinting Strengths of Diarylide Yellow(○), Barium Lithol Red(◇), and Phthalocyanine Blue(⬡) in Joncryl 67 as a Function of Milling Time

strengths of diarylide yellow, barium lithol red, and phthalocyanine blue in Joncryl 67 examined on duPont Tyvek paper are shown in Appendices C-1, C-2, and C-3, respectively. Those examined on Finch Offset paper are given in Appendices D-1, D-2, and D-3. Appendix E presents the experimental results of diarylide yellow dispersion of 8-hours milling examined on Mead Offset paper. Again, the reflectance values were taken at the maximum absorption, i.e., 400, 510, and 560 nm for yellow, red, and blue, respectively. Because of no reduction with an opaque white, the wavelengths of the maximum absorptions of these samples are different from those of the reduced inks in Part I.

The reflectance values were converted into the K/S by Equation (4b). The (K/S)-c plots of yellow, red, and blue printed on duPont Tyvek paper are shown in Figures 5, 6, and 7, respectively. Figure 5 includes the results of yellow printed on Mead Offset paper. In these figures, the pigment weight per unit area of paper is employed as abscissa instead of the printing film weight which Nippert proposed. It is obvious that the former expresses Equation (1) more correctly because the K/S is a function of the optical properties of the pigment and the paper.

It is seen in Figure 5 that four prints on Mead Offset paper have a similar K/S value regardless of the

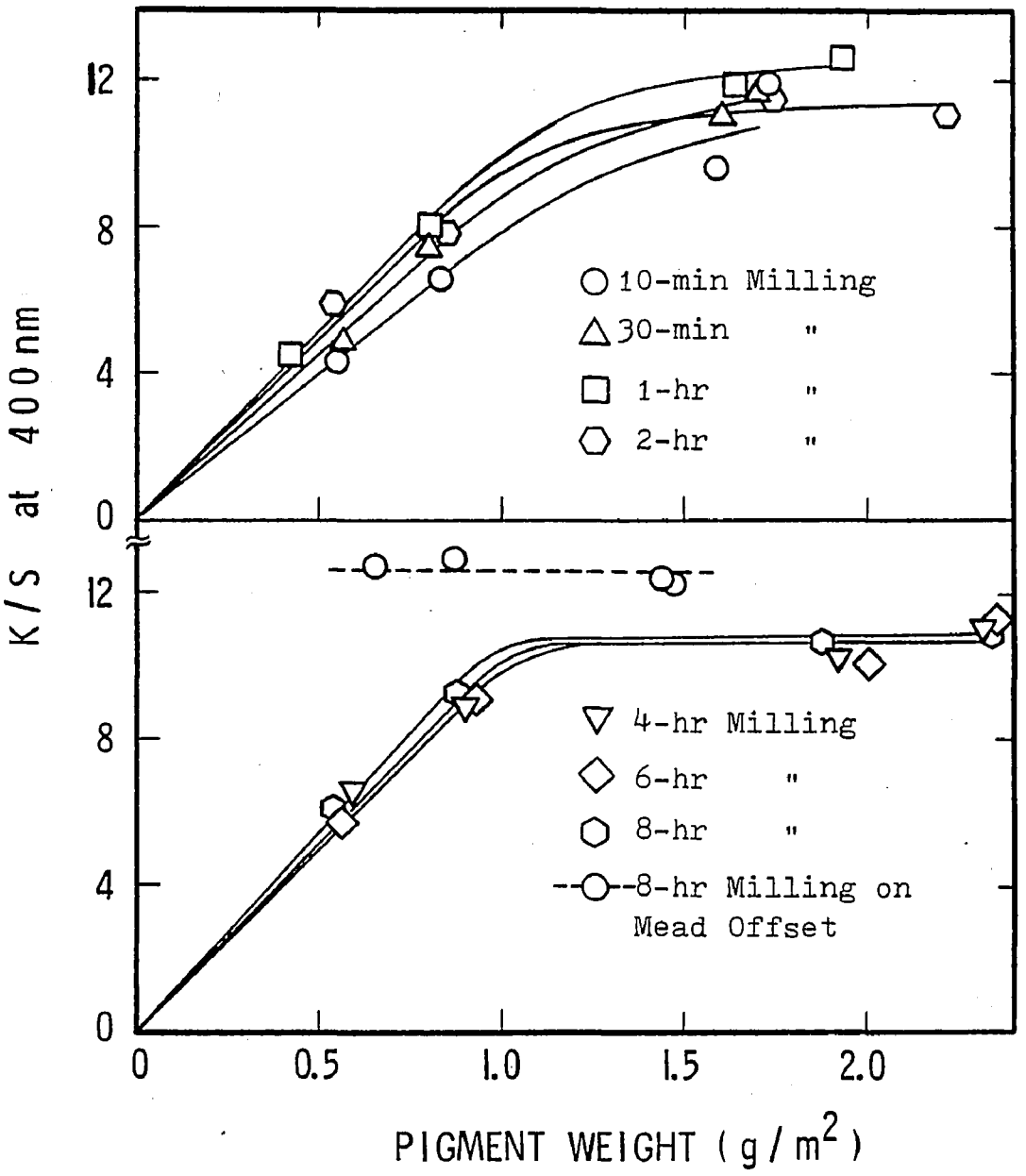

Figure 5 K/S versus Pigment Weight per Unit Area of Paper Curves for Diarylide Yellow Dispersion in Joncryl 67 printed on duPont Tyvek, analyzed by Nippert's Method

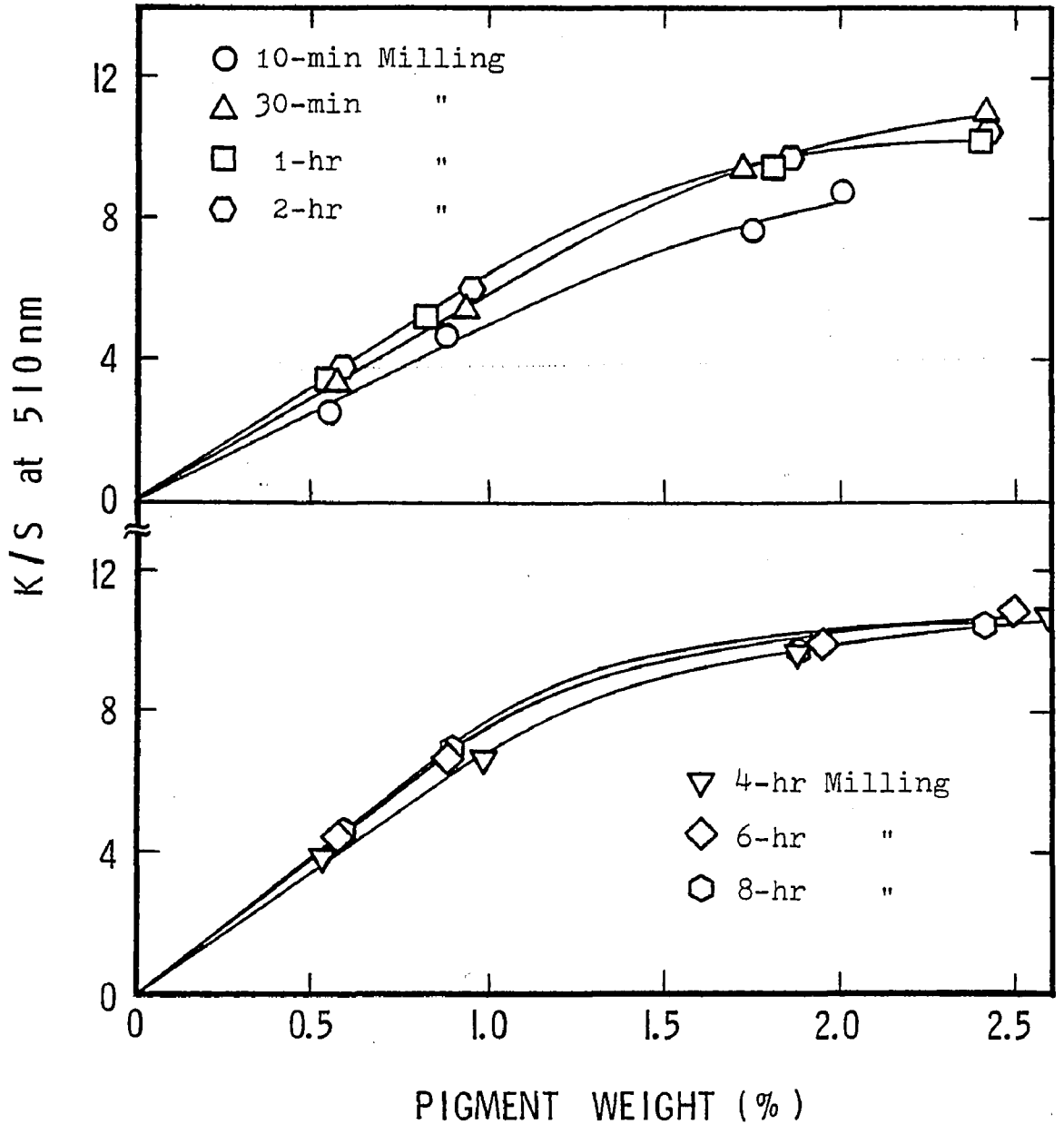

Figure 6 K/S versus Pigment Weight per Unit Area of Paper Curves for Barium Lithol Red Dispersion in Joncryl 67 printed on duPont Tyvek, analyzed by Nippert's Method

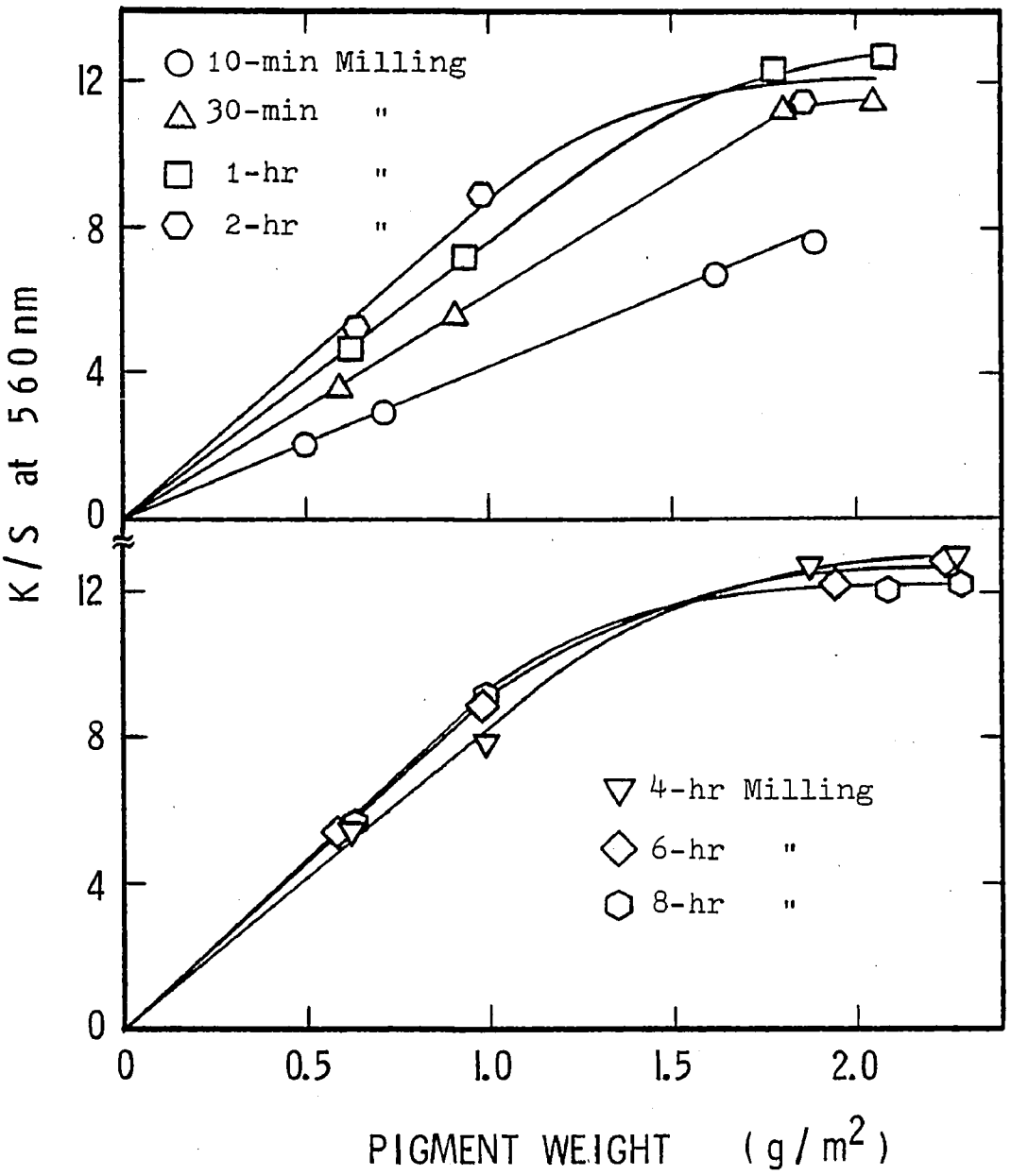

Figure 7 K/S versus Pigment Weight per Unit Area of Paper Curves for Phthalocyanine Blue Dispersion in Joncryl 67 printed on duPont Tyvek, analyzed by Nippert's Method

different pigment weights. Figure 8 gives the optical micrographs of the surfaces of three papers. The structure of fibers of duPont Tyvek and Finch Offset papers is very clear (the left side of each picture), while in the case of Mead Offset paper the texture of fibers in the top layer is visible but its outline is hazy and the fibers in the deeper part can not be observed because of the heavy coating. Also, Mead Offset paper has the very smooth surface. Hence, in the case of Mead Offset, the ink can not penetrate the paper substrate and a small amount of the ink covers the surface of the paper completely. Consequently, the reflectance values of the prints are determined only by the ink film layer on the surface of the paper and have a similar value without respect to the difference in the pigment weights.

Second, most of the curves of Figures 5, 6, and 7 show a tendency to level off at high pigment weights. It is considered that, below 1.0-1.5 g/m^2 pigment weight, the ink penetrates into the paper substrate and forms the single uniform layer predicted by Nippert, while above that weight some of the ink remains on the top of the paper, and this ink layer contributes to the reflectance of the print similar to the ink film on Mead Offset. In the region from 0 to 1.0-1.5 g/m^2 pigment weight, the linearity of the ($\underline{K}/\underline{S}$)-$\underline{c}$ curves was obtained in Figures 5, 6, and 7.

(a)

(b)

(c)

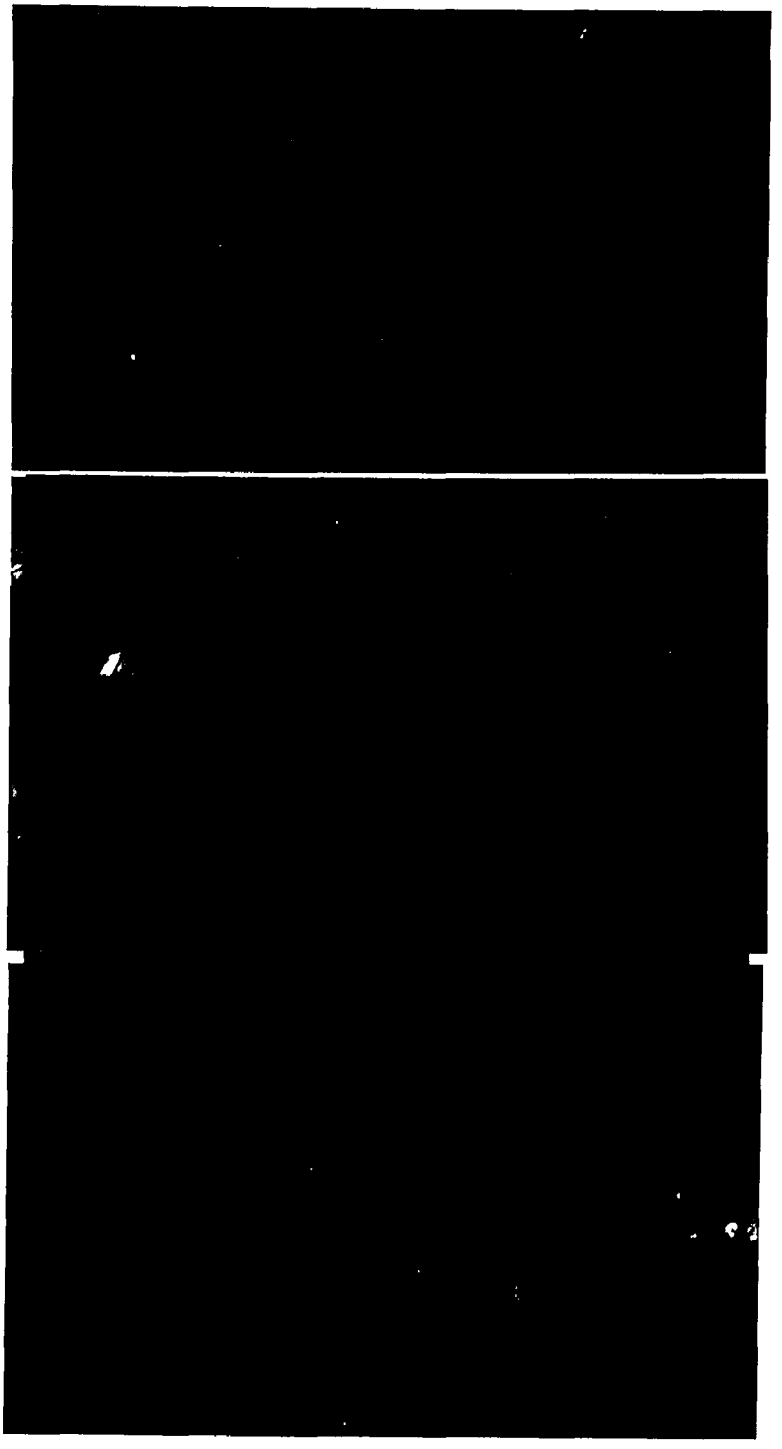

Figure 8 Optical Micrographs of Surfaces of (a) duPont Tyvek, (b) Finch Offset, and (c) Mead Offset: (x 100)

Therefore, the experimental reflectance values were used in subsequent calculations without corrections. The $\underline{k}/\underline{S}_p$ values of diarylide yellow, barium lithol red, and phthalocyanine blue in Joncryl 67 examined on duPont Tyvek paper at the different milling times were obtained graphically from Figures 5, 6, and 7, and plotted in Figure 9 as a function of the milling time.

Figures 10, 11, and 12 show the $(\underline{K}/\underline{S})$-$\underline{c}$ plots of diarylide yellow, barium lithol red, and phthalocyanine blue in Joncryl 67 printed on Finch Offset paper, respectively. Each of these plots was obtained from the experimental results of the prints made by Anilox rollers #200, 165, and 140, and does not include the result done by Anilox roller #65. All the curves are not linear but instead are concave upward. If the results of the prints made by Anilox roller #65 were plotted in these figures, the shape of the curves would be sigmoidal. Figure 13 shows the optical micrographs of blue prints at 2-hours milling printed by Anilox rollers #200, 165, 140, and 65. Some unprinted areas are visible in the prints made by Anilox rollers #200, 165, and 140 and decrease as the amount of ink increases. This phenomenon is due to the rough surface of Finch Offset paper. In the case of the print by Anilox roller #200, the unprinted area is so large that the scattering power of paper dominates and the $\underline{K}/\underline{S}$ of

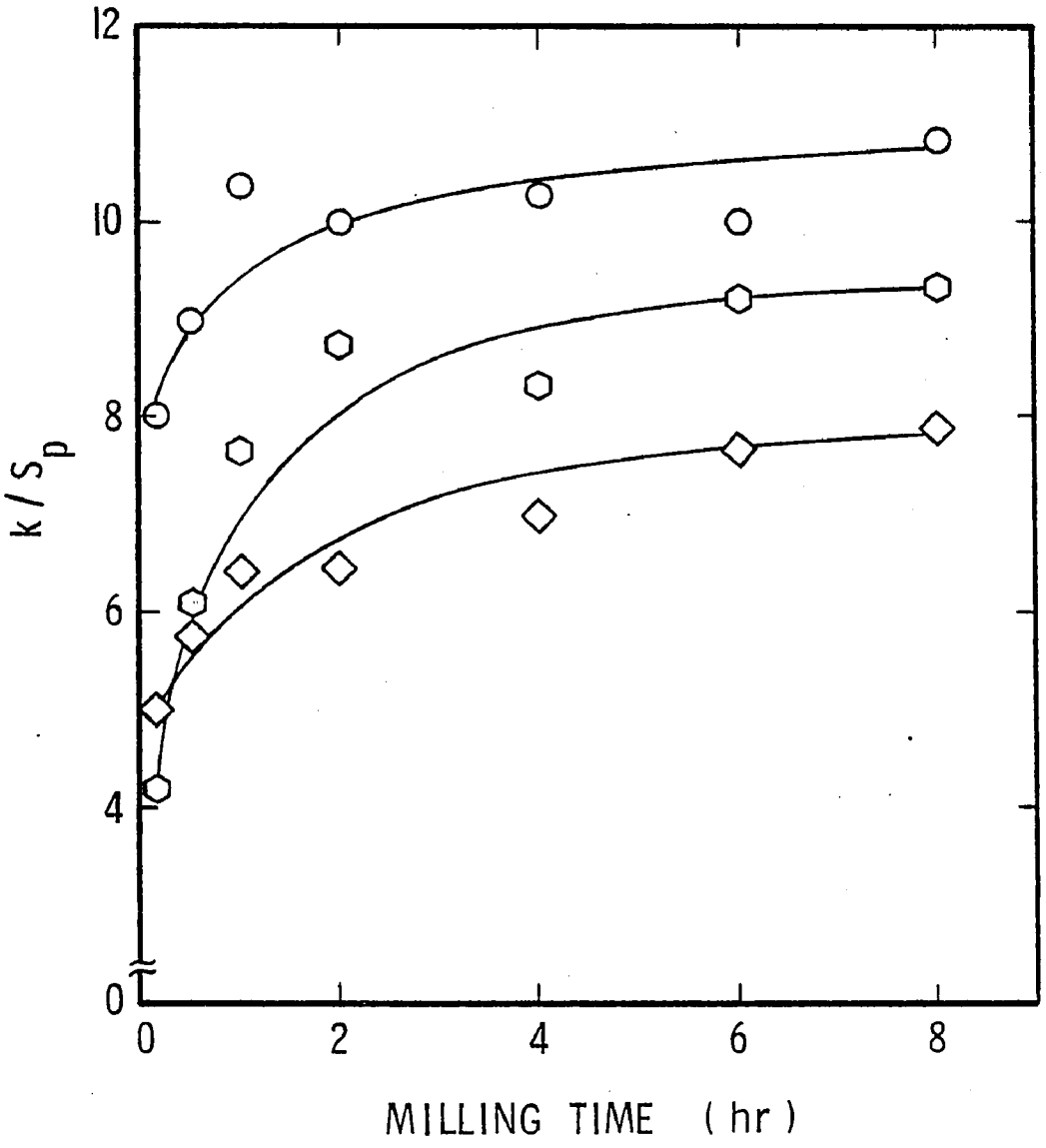

Figure 9 Printing Strengths on duPont Tyvek of Diarylide Yellow(◯), Barium Lithol Red(◇), and Phthalocyanine Blue(⬡) in Joncryl 67 as a Function of Milling Time

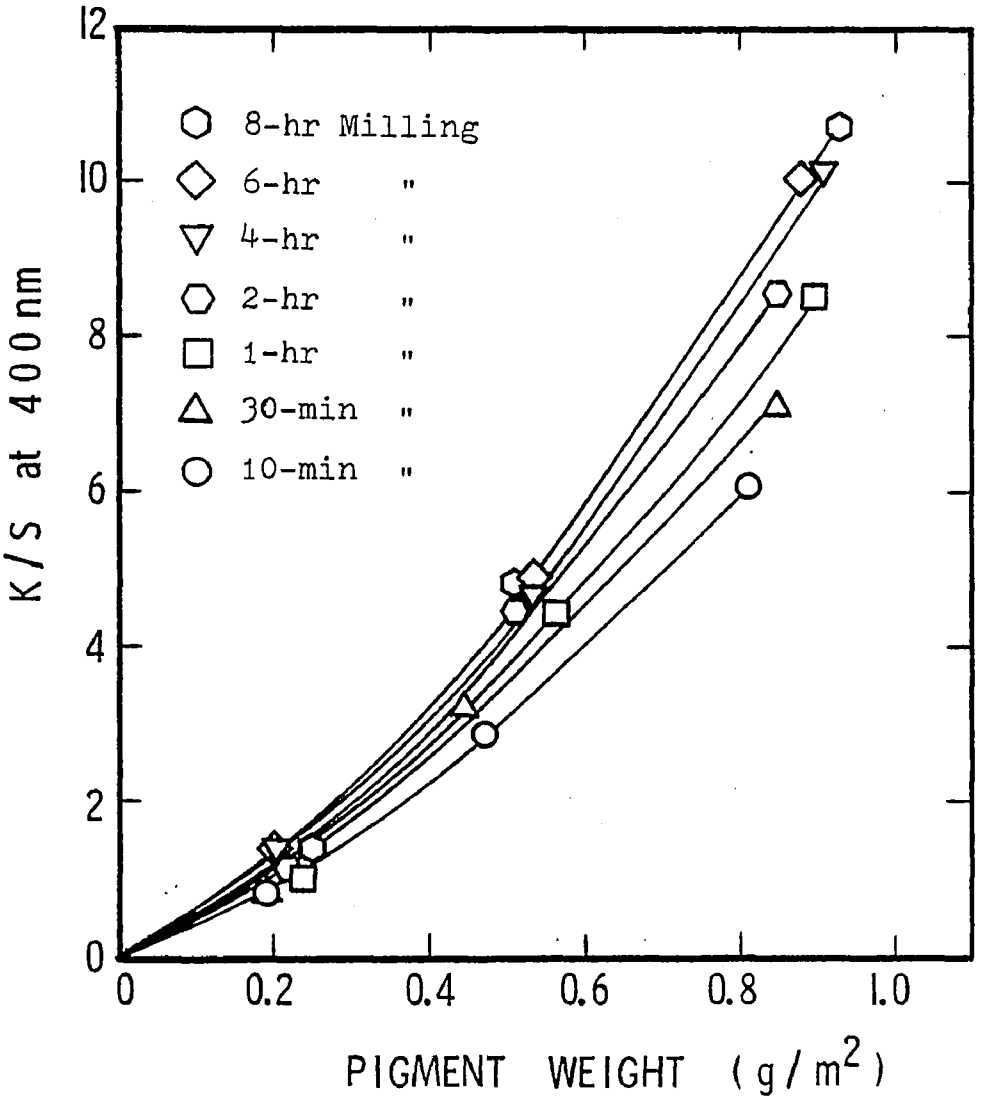

Figure 10 K/S versus Pigment Weight per Unit Area of Paper Curves for Diarylide Yellow Dispersion in Joncryl 67 printed on Finch Offset, analyzed by Nippert's Method

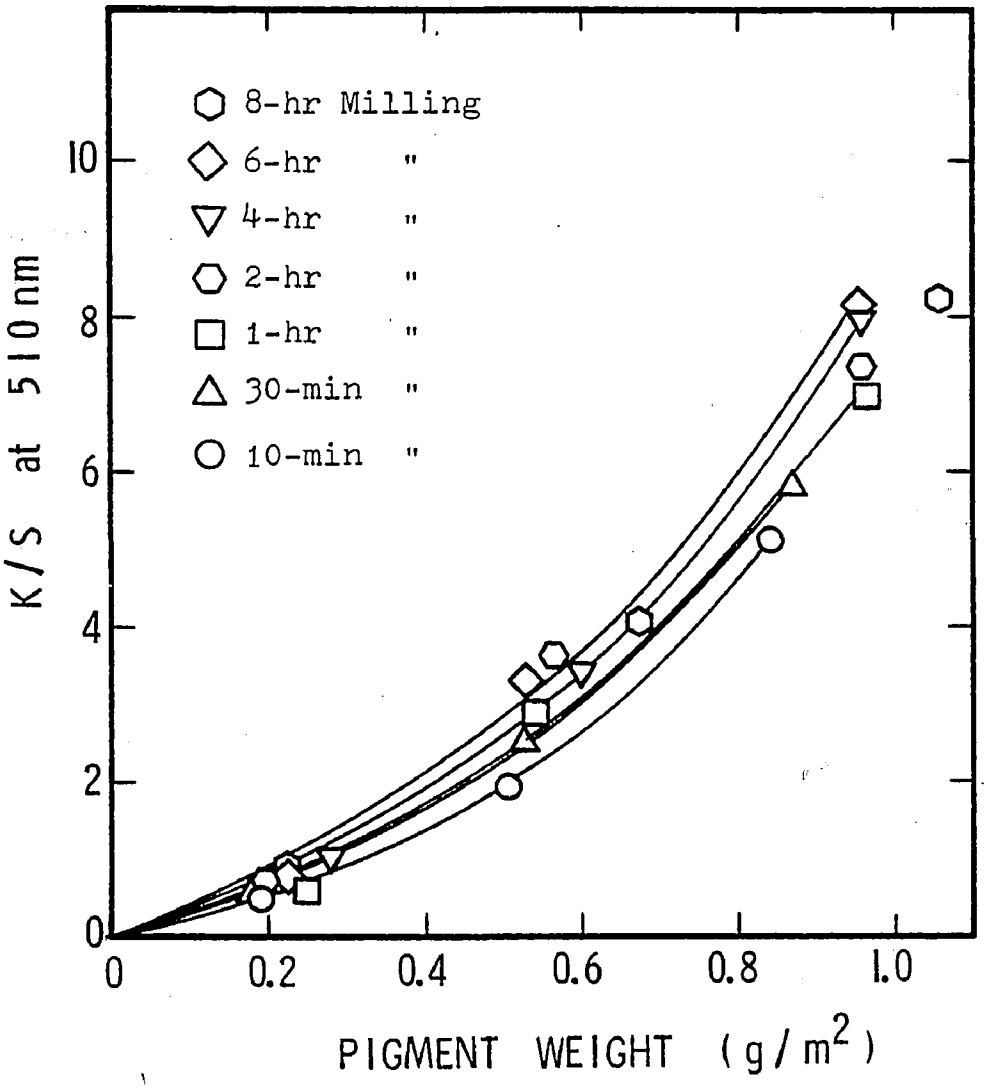

Figure 11 K/S versus Pigment Weight per Unit Area of Paper Curves for Barium Lithol Red Dispersion in Joncryl 67 printed on Finch Offset, analyzed by Nippert's Method

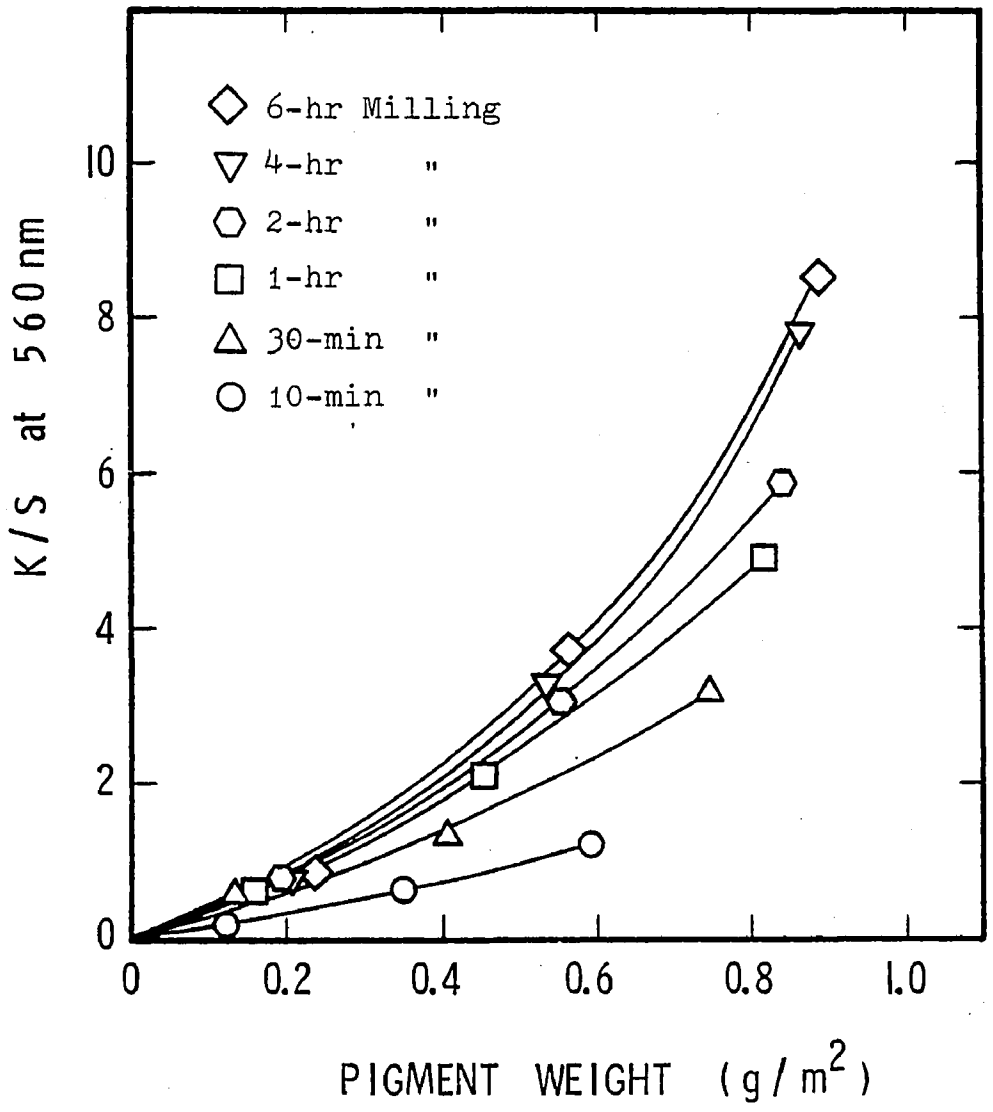

Figure 12 K/S versus Pigment Weight per Unit Area of Paper Curves for Phthalocyanine Blue Dispersion in Joncryl 67 printed on Finch Offset, analyzed by Nippert's Method

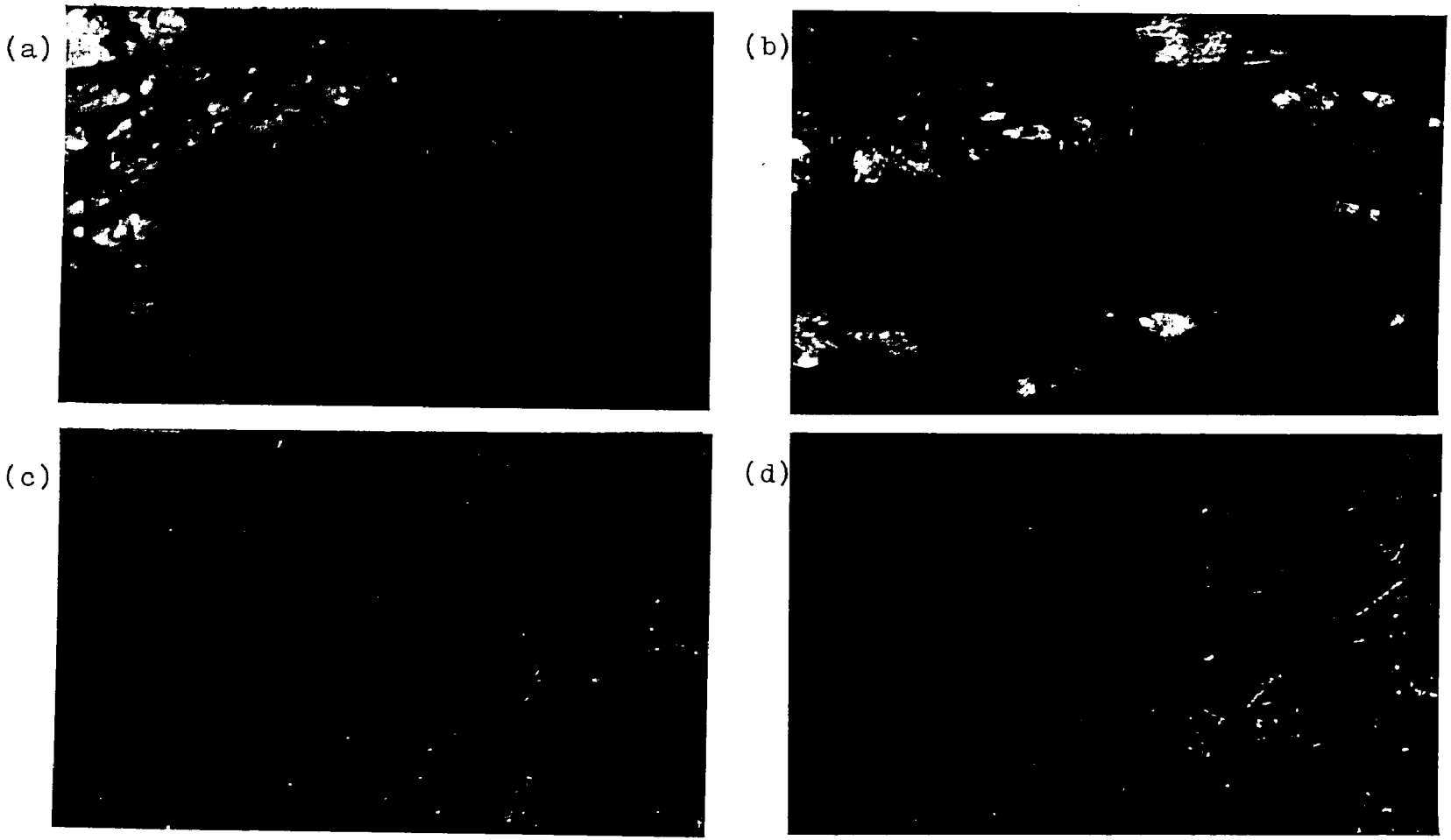

Figure 13 Optical Micrographs of Blue Prints at 2-hours Milling printed on Finch Offset by Anilox Rollers (a)#200, (b)#165, (c)#140, and (d)#65: (x 62.5)

the print appears as a small value. As the amount of ink increases, the ink penetrates the paper more uniformly and reduces the scattering power of paper. Consequently, a concave (K/S)-c curve is obtained.

Nippert noticed this situation in his work and set up the three-layer model[6] based on the following Walker-Fetsko equation[13] on the ink transfer from the printing plate to the paper:

$$F = (1 - e^{-mz}) , \qquad (10)$$

where F = the contact area of the ink on the plate with the paper

z = the weight of the ink on the plate

m = the Walker-Fetsko coverage parameter.

In this model, the values of z must be given, which is unknown in the present work. Furthermore, both the three-layer model and the Walker-Fetsko equation were established for the paste inks, and therefore, may not be applicable to the present case. That is, although the Walker-Fetsko coverage parameter, m, must be a constant for the same system, it did not remain constant with increasing ink weight in the present work. Ichikawa et al.[14] already pointed out that the value of m is not a constant but increases with increasing ink layer thickness on the plate, especially in the case of the print on rough papers.

Instead, the prints made by the same Anilox roller at

the different milling times were compared. It was found that, in the prints made by Anilox roller #140, the unprinted area is so small that its effect can be neglected and Equation (1) could be valid. Figure 14 gives the printing strengths of three pigments as a function of the milling time, in which the $\underline{k}/\underline{S}_p$ values were calculated simply by dividing the $\underline{K}/\underline{S}$ by the pigment weight, $\underline{c}$, with respect to the prints made by Anilox roller #140. Surprisingly, very reasonable curves were obtained.

Comparison of printing strengths in Figures 9 and 14 with tinting strengths in Figure 4 gives good agreement with regard to the rate of increase in color strengths of three pigments. Phthalocyanine blue shows a very sharp increase in its color strength, and diarylide yellow and barium lithol red show small (compared with phthalocyanine blue) but considerable increases in their color strengths. This difference of the rate of increase in color strength between these pigments may be due to two reasons: (i) the variation of an amount of work required to wet the surface of pigments and break down the agglomerates of these pigments; (ii) the difference of their optical constants, i.e., absorption coefficient and refractive index. At 10-minutes milling, it was observed that phthalocyanine blue dispersion still contained very large agglomerates (about 0.1 mm in size), while such large agglomerates were hardly

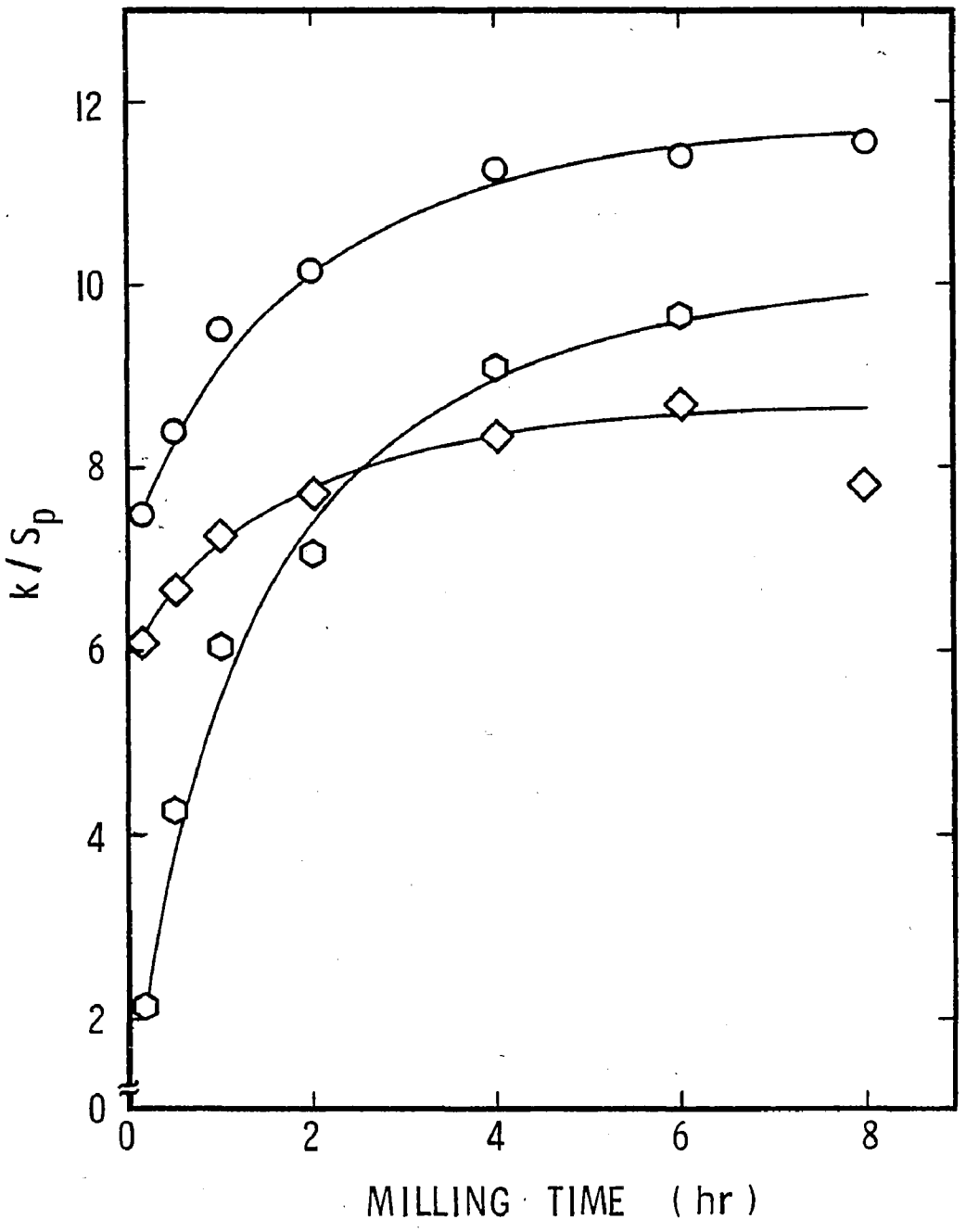

Figure 14 Printing Strengths of Diarylide Yellow (○), Barium Lithol Red(◇), and Phthalocyanine Blue (⬡) in Joncryl 67 as a Function of Milling Time; Results obtained from Anilox Roller #140 Prints on Finch Offset by Nippert's Method

found in diarylide yellow and barium lithol red dispersions. Therefore, it is considered that a greater amount of work is necessary for wetting and mechanical disruption of phthalocyanine blue pigment. The second reason was explained by Brockes[15]. He expressed color strength as a function of particle size from Mie theory for colored pigments which have different absorption coefficients, $\underline{k}$, and refractive indexes, $\underline{n}$. He pointed out that: (i) the pigments which have a very high $\underline{k}$ value and a rather low $\underline{n}$ value ($\simeq 1$), e.g., carbon black, show very rapid increases in color strength with decreasing particle size until the particles are reduced to 0.05 μm in size; (ii) the pigments which have a relatively high $\underline{k}$ value and a rather low $\underline{n}$ value, e.g., most azo pigments, show moderate increases in color strength with decreasing particle size up to about 0.1 μm in size; (iii) the pigments which have a low $\underline{k}$ value and a high $\underline{n}$ value, e.g., most inorganic pigments, show slow increases in color strength and an optimum particle size at about 0.2 μm.

Carr reported a rapid increase in the color strength of phthalocyanine blue with decreasing particle size[4]. He found that the color strength of phthalocyanine blue slowly increases until the mean particle size becomes equal to 0.4 um, and then, it becomes very sensitive to small changes in the particle size and rises very sharply until

the mean size is down to 0.125 μm.

Thus, phthalocyanine blue belongs to the first group of the Brockes classification, and diarylide yellow and barium lithol red are classified in the second group. It is well known that these two pigments are typical azo pigments.

It is noticed from Figures 4, 9, and 14 that it takes more than 4 hours before color strengths reach the maximum values. Therefore, the ball-milling times on the Red Devil Paint Shaker normally used in industry, from 15 to 30 minutes, may be much too short to obtain the sufficient dispersion of the pigments, although the exact times to get the sufficient dispersion will depend on the ink formulations and other milling conditions. Carr pointed out in his work with the sand mill[16] that complete dispersion of the pigment is not achieved even after 8 hours of sand grinding, and he suggested a similar conclusion on the milling times.

The maximum values of color strengths after 4-hours milling represent either: (i) the equilibrium state of the particle size; or (ii) the final values of only color strengths, and the particles are still becoming smaller. In the latter case, color strength has become independent of the particle size. This is readily understandable. Since the particle is very small at the maximum value of

color strength, the substrate within the particle has the same absorption effect as that in the surface regions, because the individual particle is still transparent. Thus, further size reduction can not yield additional absorption and therefore unnecessary. Huwart[17] carried out the same experiment on Permanent Yellow GR11-1300 and measured the mean particle size by capillary chromatography and electron microscopy. According to his results, the mean particle size of this pigment after 4-hours milling is 0.44 μm and still becomes smaller gradually. Therefore, the maximum value of color strength of this yellow pigment represents the latter case. The former case, i.e., the equilibrium state of the particle size, has also been observed many times. Several examples will be discussed in Part II.

Part II. Variation of Type of Resin

The ability of Nippert's method to distinguish the dispersion state of the same pigment dispersions in the different resin systems was investigated in this part.

The experimental data and results for tinting strength of diarylide yellow dispersions in Joncryl 678, and Cropolamid 18W26 and 18W58, are given in Appendices F-1, F-2,and F-3, respectively. Those for printing strength of diarylide yellow dispersions in Joncryl 678,

and Cropolamid 18W26 and 18W59, are given in Appendices G-1, G-2, and G-3, respectively.

Tinting strength ($\underline{k}/\underline{s}$) and printing strength ($\underline{k}/\underline{S}_p$) were estimated in the same processes as in Part I. The results are shown in Figures 15 and 16, and compared with the Joncryl 67 system.

Comparison of Figures 15 and 16 gives good agreement with respect to the order of pigment-dispersing power of resins. Both figures show that Joncryl 67 has the best pigment-dispersing power, followed by Joncryl 678 and Cropolamid 18W26. However, it is noticed that tinting strength expresses the dispersing power difference between resins more significantly than printing strength. This tendency of tinting strength may give the more distinct information on the pigment-dispersing power of resins. However, since printing strengths are obtained from proof prints, printing strengths of the different resin systems may show the real difference between their appearances which will be obtained on examination of prints by the human eye.

The difference of color strengths between these resin systems in both Figures 15 and 16 is clearly a result of the variation of the pigment particle size in these resin systems. The dispersion process is generally divided into three distinct stages: first, wetting, in which the

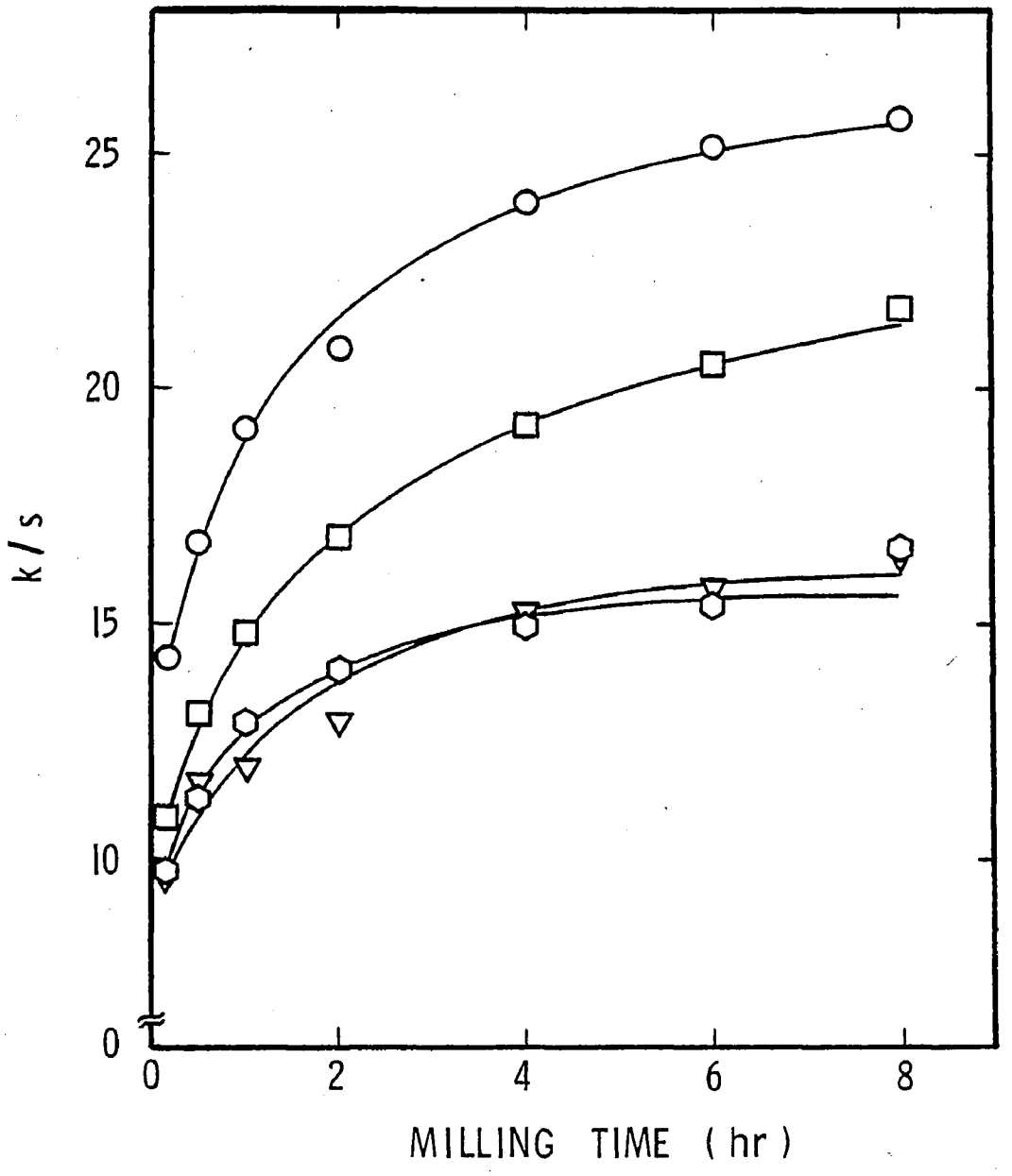

Figure 15 Tinting Strengths of Diarylide Yellow in Joncryl 67(○), Joncryl 678(□), Cropolamid 18W26(⬡), and Cropolamid 18W58(▽) as a Function of Milling Time

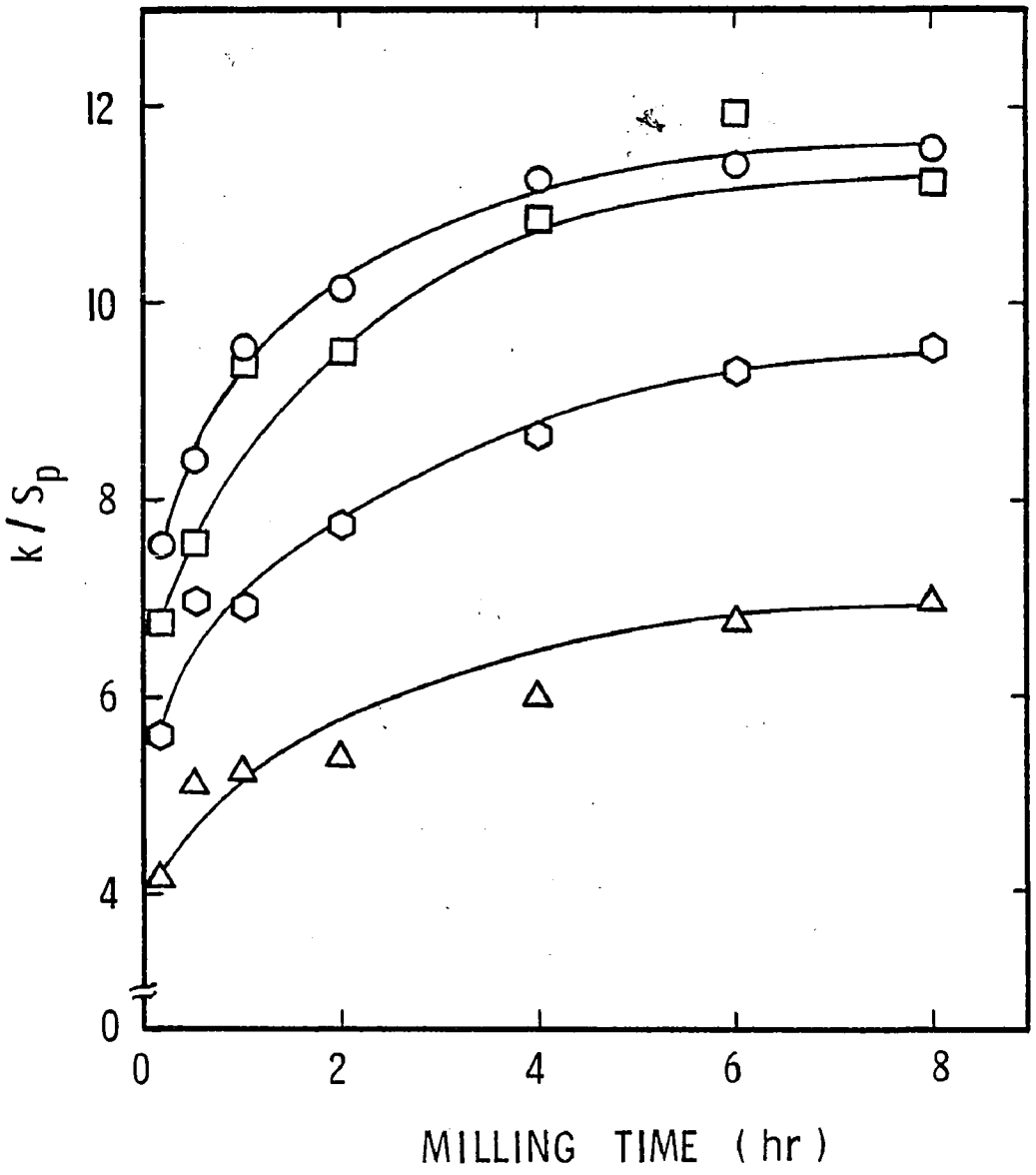

Figure 16 Printing Strengths of Diarylide Yellow in Joncryl 67(○), Joncryl 678(□), Cropolamid 18W26(⬡), and Cropolamid 18W59(△) as a Function of Milling Time; Results obtained from Anilox Roller #140 Prints on Finch Offset

pigment/air interface is replaced by the pigment/medium interface; second, mechanical disruption, in which most agglomerates are broken down into smaller particles; and third, stabilization of the resulting dispersion against flocculation. Among these three stages, the stabilization of the dispersed partilces is considered to have the largest effect on the final particle size. Dispersion mechanism is described in many papers[18-21], and therefore, only the third stage will be reviewed briefly in the following.

When the pigment particles in an unstabilized dispersion approach one another as a result of their Brownian motion, van der Waals attraction forces increase with decreasing inter-particle distance, and thus rapid flocculation occurs, as expressed mathematically by Smoluchowski [22]. To prevent this flocculation in the pigment dispersion, the resin molecules must be adsorbed on the surface of the pigments and build up an adsorbed layer, which gives rise to electrostatic or steric repulsion.

For the case of resins which have ionic charges in their molecules, the particles are given the surface charge by the adsorption of resin molecules. This surface charge and the atmosphere of counterions constitute the electrical double layer around the particle. When such particles approach one another, their electrical double layers

overlap, and the repulsive potential energy arises from the work that must be done to remove the counterions from between the particles so that they can get closer to one another. Two equations are shown below, both of which were derived for spherical particles and small surface potential [23]. First, for system of large particles with moderate electrolyte concentration ($\kappa a \gg 1$):

$$V_R = \frac{\epsilon a \psi_o^2}{2} \ln[1 + \exp(-\frac{H}{1/\kappa})], \qquad (11a)$$

while for small particles with very low electrolyte concentration ($\kappa a \ll 1$):

$$V_R = \frac{\epsilon a \psi_o^2}{(H/a) + 2} \exp(-\frac{H}{1/\kappa}) , \qquad (11b)$$

where V_R = the repulsive potential energy

ϵ = the dielectric constant of the dispersion medium

a = the radius of the particle

ψ_o = the surface potential of the particle

H = the separation of the surfaces of particles

$1/\kappa$ = the thickness of the diffuse double layer.

On the other hand, steric repulsion depends largely on the physical and chemical natures of the adsorbed resin molecules. Several mechanisms have been proposed for steric repulsion, although there are arguments between investigators against accepting some of these mechanisms [24-28]. First, the effect of the adsorbed layer on van

der Waals attractive forces between particles must be considered. As Vold showed theoretically[29], a significant reduction in the magnitude of the attractive forces is possible, because the distance between the surfaces of particles, when they collide, is increased by twice the thickness of the adsorbed layer. Second, as two particles approach each other and the interpenetration of two adsorbed layers begins, a repulsion resulting from the change of the free energy due to the mixing of the adsorbed polymeric clouds is expected[25,26,30]. Third, when the particles get closer to each other, the compression of the adsorbed layers occurs, and consequently the configurational entropy of the adsorbed resin molecules decreases. This decrease of entropy will lead to a repulsive energy [26,31-33].

Therefore, it is obvious that both electrostatic and steric repulsion contributes to the stabilization of most pigment dispersion. In general, steric repulsion appears in a shorter range than electrostatic repulsion and increases very rapidly with decreasing inter-particle distance. Combination of electrostatic and steric repulsive potential energies and van der Waals attractive potential energy results in the total potential energy of interacting two particles as a function of the distance between them. The pigment dispersion which has relatively

high repulsive potential energies shows the maximum at a certain distance in its total potential energy curve, which is so-called the potential energy barrier and the height of which is directly related to the stability of the dispersion. For a stable system, the barrier must be at least 15-20 times the thermal energy of the particles.

In order to obtain a sufficiently high energy barrier, the following physical and chemical properties may be necessary for the resin molecules: (i) reasonable balance of hydrophobic and hydrophilic portions in the molecule, because the adsorption of resin molecules will occur only when the adsorption energy is sufficient to compensate for the loss of energy which the molecules experience on leaving the bulk solution; (ii) the high ionic charge; Equations (11a) and (11b) show that electrostatic repulsive energy is proportional to the square of the surface potential which increases with increasing surface charge; (iii) the high interaction between the resin molecules and the solvent; from the thermodynamic point of view, the number of the conformations which a resin molecule can adopt on the pigment surface is much greater in a good solvent than in a poor solvent and therefore a resin molecule will adsorb with a higher energy; furthermore, in a good solvent, a resin molecule may strech out its chain segment more freely into the bulk solution;

(iv) high molecular weight and high flexibility; the number of the conformation of a resin molecule on the pigment surface is also a strong function of the molecular weight and flexibility; the resin molecules consisting of long linear chains will show higher stabilization than bulky molecules; moreover, the thickness of the adsorbed layer is increased with increasing molecular weight; however, it should be noticed that, if the resin content in an ink is constant, the viscosity of the ink is also increased as the molecular weight of the resin increases; too high a viscosity may result in a low content of pigment and resin in a diluted ink, and hence, low color strength, poor gloss, and many kinds of poor resistance; (v) the wide size distribution of the chain segment in a resin molecule; a resin molecule adsorbed on the pigment particle will form a train-loop or an anchor-trail structure with a certain size distribution; Hesselink et al. showed theoretically that the broader size distribution of loops or trails give the higher steric repulsive energy to the system[26]; (vi) the strong interaction between the pigment surface and resin molecules; the strong pigment-resin interaction, which may be represented by the solubility parameter or the acid-base concept[34,35], will result in high adsorption energy, and also, reduce desorption of adsorbed resin molecules which occurs on approach of particles; (vii)

there are many other factors which control the stability of pigment particles, e.g., the structure of a resin molecule (random, block, or graft), the pigment-solvent interaction, or the resin concentration, etc.

Figures 15 and 16 clearly indicate that the Joncryl resins have the higher stabilizing power for diarylide yellow pigment than the Cropolamid resins. Table 7 gives the type and several properties of Joncryl 67 and 678, and Cropolamid 18W26, 18W58, and 18W59.

If it is assumed that the same amount of resin molecules is adsorbed on the pigment particle, the high acid number of the Joncryl polymers will give the higher surface potential to the pigment particle and consequently higher electrostatic repulsive potential energy to the system than the Cropolamid resins.

The Joncryl polymers are made from styrene, and ethylenically unsaturated carboxylic acid or anhydride of half ester, or ethylenically unsaturated ester monomers by chain polymerization. Therefore, it is expected that each unit is arranged rather regularly in a molecule in proportion to the amounts of these monomers. Especially, pendant carboxyl groups can be located at any position in a polymer molecule. On the other hand, the Cropolamid resins are made from polyamides and dimer acids (C_{36}), manufactured from fatty acids, by condensation polymerization. Thus,

Table 7

Properties of Joncryl 67 and 678, and
Cropolamid 18W26, 18W58, and 18W59

	Joncryl		Cropolamid		
	67	678	18W26	18W58	18W59
Type of Resin	Styrene-Acrylic		Polyamide*		
Acid Number	200	200	100	130	100
Amine Number	-	-	8	8	8
Vehicle Viscosity**	210cps	60cps	120cps	1200cps	800cps
(Resin Content)	(27.5%)	(27.5%)	(25%)	(22%)	(25%)

* Cropolamid resins are the reaction products of dimer acids with polyamides.

** Viscosity was measured at 25°C. Cropolamid 18W26 and 18W59 vehicles contain 15 wt % isopropyl alcohol.

most carboxyl groups may exist at ends of polymer molecules. Because of this one-sided distribution of the carboxyl groups and the low acid number, the amount of carboxyl groups is not sufficient to make a neutralized Cropolamid molecule perfectly water-soluble except Cropolamid 18W58. Hence, it may be inferred that Joncryl polymer molecules can adopt an expanded conformation on the pigment particle, while in the case of Cropolamid resins the large middle segment in a polymer molecule which is highly hydrophobic coils up tightly on the particle and only the short segments with carboxyl groups protrude into the solution. Therefore, much higher steric repulsive potential energy may be expected for the Joncryl systems than for the Cropolamid systems.

As mentioned previously, the theory predicts that a molecule of higher molecular weight gives better stability. It is seen in Table 7 and Figures 15 and 16 that Joncryl 67 has a higher viscosity than Joncryl 678 and shows higher color strength. Although the difference of molecular weight will be one of the reasons for the difference of the stabilizing power between Joncryl 67 and 678, the variation in their resin formulations may affect their pigment-stabilizing powers more strongly. Cropolamid 18W26 and 18W58 did not show too much difference between their color strengths. Comparison of Cropolamid 18W26 and 18W59 shows

a discrepancy in the theoretical prediction regarding the molecular weight effect. However, it is considered that the resin-solvent interaction has a much strong influence on their pigment-stabilizing powers. A neutralized Cropolamid 18W59 molecule may have much less interaction with water than a neutralized Cropolamid 18W26 molecule because of its higher molecular weight and the same acid number.

According to Sorensen[35], diarylide yellow pigment usually shows an amphoteric or basic property, although even chemically related pigments can possess different properties due to the different conditions of manufacture for the pigments and the different finishing treatment. If the Permanent Yellow GR11-1300 used in the present work is basic, the Joncryl polymers will have a stronger interaction with this pigment than the Cropolamid resins, because the Joncryl polymers are considered to be more acidic and the Cropolamid resins may have a basic nature due to the amide and amine groups.

The relative effect of the variation in the ink formulations should be mentioned. On investigation of the resin effect on printing strength, the pigment-resin ratio was changed in the different resin systems in order to keep their viscosities constant. It is known that the resin concentration affects the amount of the resin adsorption,

and that, at a very low concentration, there is a possibility that parts of the adsorbed molecules become attached to two or more particles, bringing about flocculation by the bridging mechanism. However, as the resin concentration increases, the amount of the adsorption tends to level off and becomes independent of the change of the concentration. This is the region of the resin contents which is usually employed in the ink formulations. Crowl pointed out that maximum adsorption of the resin molecules, even on quite different pigments, is frequently in the range of 1.5-2.0 mg resin/m^2 pigment surface[20]. If the Permanent Yellow GR11-1300 has a surface area of 100 m^2/g, 2.1-2.8 g of resin are required for 14 g of this pigment. In the present case, even the Cropolamid 18W59 system contains 8.5 g resin/14 g pigment, and this amount is sufficient to give the pigment particles the best stability which can be obtained with Cropolamid 18W59. Therefore, the variation in the pigment-resin ratios may not have a meaningful bearing on the pigment dispersion but may affect other ink properties, e.g., gloss, durability, and rub-resistance, etc.

The DLVO theory which describes the electrostatic stability theoretically predicts that under the same condition the larger colloidal particles have the higher potential energy barrier and therefore are more stable than the

smaller colloidal particles[20,23]. On the other hand, Hesselink et al. showed theoretically that the steric stability is inversely proportional to the particle radius and therefore decreases with increasing particle size[26]. Generally, in the pigment dispersion the mean particle size decreases with increasing pigment-stabilizing power of the resin molecules. This is understandable from a kinetic point of view. The smaller particles require a higher potential energy barrier to be stabilized than the larger particles[23]. The final mean particle size will be decided by a combination of electrostatic and steric stabilities. Any resin molecule will exert its maximum stabilizing action when adsorbed on to a particle of a certain size, because of the opposite tendency between electrostatic and steric stabilities with respect to the particle size.

In the present work, the resin effect on the degree of pigment dispersion was investigated only on diarylide yellow because it was not the main objective. There is a possibility that the other pigments show the different order of the pigment-stabilizing power of resins due to the different pigment-resin interaction[35,36].

FUTURE STUDIES

The new color strength method is subjected to some difficulty and limitation on analysis of printing strength of the prints on Finch Offset paper, that is, the non-linearity of the (K/S)-c plots was caused by the rough surface of the paper and the subsequent reflectance of the unprinted area. Hence, another model which takes into account the above situation must be developed.

As mentioned before, Nippert noticed this problem and developed the three-layer model to consider the surface roughness of paper. Unfortunately, because the different printing instruments were used in the present work and the properties of inks are quite different from those in Nippert's research, this model can not be applied to the present study.

Thus, in order to correct the non-linear (K/S)-c curves, it is desirable to develop the relationship between the fraction of printed area on paper and the pigment weight per unit area of paper using a more sophisticated printing instrument.

CONCLUSION

It was found that the choice of paper substrate affected the linearity of the ($\underline{K}/\underline{S}$)-$\underline{c}$ plots. With a smooth-surfaced coated paper (Mead Offset), the color strength did not vary with pigment weight, because the paper is solidly coated and most of the ink remains on the surface of paper and this layer mainly determines the reflectance. For a porous synthetic polyolefin paper (duPont Tyvek), the ($\underline{K}/\underline{S}$)-$\underline{c}$ plots were linear up to 0.1-0.15 g/m^2 pigment weight, where the basic assumption that the ink penetrates the paper substrate to form a single uniform layer holds because of the appropriate smoothness and the reasonable porosity of this paper. The color strengths increased with increasing milling time up to 4-hours milling. Moreover, the color strengths of prints varied characteristically for different pigments. For a lighter coated paper (Finch Offset), the ($\underline{K}/\underline{S}$)-$\underline{c}$ were not linear, but instead were concave upward: this variation was attributed to the rougher surface of this paper. However, for prints of comparable pigment weights, the same tendency of changes in color strengths as those on duPont Tyvek was obtained.

It was also demonstrated that the new color strength method clearly distinguished the pigment-stabilizing power

difference in various resins.

Thus, the new method offers promise as a routine measurement for degree of dispersion.

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APPENDICES

Appendix A-1

Exerimental Data & Results for Tinting Strength at 440nm of Diarylide Yellow Dispersion in Joncryl 67

Milling Time	Pig. Conc. (%)	R_m (%)	R_t (%)	K/S	k/s
10 min	1.14	36.87	56.92	0.163	
	2.08	29.76	48.31	0.277	
	5.00	19.11	32.54	0.699	
	9.92	12.89	21.23	1.461	14.3
30 min	0.95	37.47	57.59	0.156	
	1.97	27.93	45.87	0.319	
	4.97	17.57	29.91	0.821	
	9.72	12.08	19.61	1.648	16.7
1 hr	1.13	33.45	52.94	0.209	
	1.86	27.20	44.87	0.339	
	6.96	13.66	22.73	1.313	
	11.90	10.03	15.36	2.332	19.1
2 hr	1.05	32.98	52.37	0.217	
	2.35	24.71	41.32	0.417	
	4.37	16.88	28.70	0.886	
	10.40	10.36	16.06	2.194	20.8
4 hr	1.21	29.42	47.87	0.284	
	2.05	23.12	38.95	0.478	
	4.83	15.07	25.41	1.095	
	9.88	9.82	14.91	2.428	23.9
6 hr	1.00	30.50	49.27	0.261	
	1.89	22.91	38.63	0.487	
	5.03	13.95	23.29	1.263	
	9.93	9.64	14.52	2.516	25.1
8 hr	1.13	28.68	46.88	0.301	
	2.07	21.75	36.83	0.542	
	4.90	13.97	23.33	1.260	
	9.55	9.77	14.80	2.452	25.7

Appendix A-2

Experimental Data & Results for Tinting Strength at 560nm of Barium Lithol Red Dispersion in Joncryl 67

Milling Time	Pig. Conc. (%)	R_m (%)	R_t (%)	K/S	k/s
10 min	1.12	37.86	58.02	0.152	
	2.32	27.77	45.65	0.324	
	4.76	19.45	33.11	0.676	
	10.82	12.27	19.99	1.601	14.5
30 min	1.26	33.10	52.52	0.215	
	2.21	26.23	43.51	0.367	
	5.23	16.82	28.59	0.892	
	10.27	11.64	18.72	1.765	17.1
1 hr	0.96	36.44	56.44	0.168	
	2.33	24.55	41.09	0.422	
	5.20	16.04	27.19	0.975	
	10.92	10.71	16.80	2.060	18.5
2 hr	1.21	31.97	51.13	0.234	
	1.99	25.46	42.41	0.391	
	5.62	14.85	24.99	1.126	
	10.73	10.54	16.44	2.124	19.9
4 hr	1.00	33.71	53.26	0.205	
	1.86	25.04	41.81	0.405	
	5.15	15.04	25.35	1.099	
	10.62	10.23	15.78	2.247	21.2
6 hr	1.41	28.37	46.47	0.308	
	2.01	24.16	40.51	0.437	
	5.56	14.14	23.65	1.232	
	10.56	10.11	15.53	2.297	21.9
8 hr	1.39	28.11	46.12	0.315	
	2.28	22.17	37.49	0.521	
	5.14	14.45	24.24	1.184	
	10.46	9.94	15.17	2.372	22.7

Appendix A-3

Experimental Data & Results for Tinting Strength at 610nm of Phthalocyanine Blue Dispersion in Joncryl 67

Milling Time	Pig. Conc. (%)	R_m (%)	R_t (%)	K/S	k/s
10 min	1.04	39.27	59.56	0.137	
	2.91	25.20	42.04	0.400	
	5.30	18.46	31.44	0.748	
	8.09	14.27	23.90	1.212	14.4
30 min	1.43	26.20	43.47	0.368	
	1.97	22.29	37.82	0.511	
	5.02	13.43	22.29	1.355	
	10.82	8.63	12.31	3.123	27.8
1 hr	1.12	26.37	43.71	0.362	
	2.40	18.07	30.78	0.778	
	5.32	11.64	18.72	1.765	
	10.48	8.13	11.19	3.524	33.5
2 hr	1.13	24.36	40.81	0.429	
	2.25	17.17	29.21	0.858	
	5.36	10.47	16.29	2.151	
	10.51	7.46	9.66	4.224	40.0
4 hr	1.22	21.89	37.05	0.535	
	2.58	14.77	24.84	1.137	
	6.03	9.29	13.76	2.703	
	9.83	7.29	9.27	4.440	44.7
6 hr	1.45	19.46	33.13	0.675	
	2.41	14.99	25.26	1.106	
	4.94	9.28	13.74	2.708	
	9.89	7.12	8.88	4.675	47.2
8 hr	1.15	21.35	36.20	0.562	
	1.99	16.07	27.24	0.972	
	5.57	9.17	13.50	2.771	
	10.47	6.99	8.58	4.870	48.0

Appendix B

K/S of Titanium Dioxide in Joncryl 67

Wavelength (nm)	R_m (%)	R_t (%)	(K/S) $x10^3$
440	84.88	93.08	2.57
560	88.87	95.04	1.18
610	89.35	95.27	1.17

Appendix C-1

Experimental Data & Results for Printing Strength at 400nm of Diarylide Yellow in Joncryl 67 printed on duPont Tyvek

Milling Time	Anilox Roller#	Pigment Weight (g/m^2)	R (%)	K/S	k/S_p
10 min	165	0.543	9.35	4.39	
	140	0.829	6.60	6.61	8.04
	65	1.586	4.69	9.68	
	36	1.733	3.88	11.91	
30 min	165	0.562	8.56	4.88	
	140	0.795	5.97	7.41	9.00
	65	1.600	4.14	11.10	
	36	1.695	3.93	11.74	
1 hr	165	0.419	9.10	4.54	
	140	0.800	5.53	8.07	10.38
	65	1.633	3.88	11.91	
	36	1.924	3.67	12.64	
2 hr	165	0.529	7.23	5.95	
	140	0.843	5.68	7.83	10.00
	65	1.738	3.98	11.58	
	36	2.210	4.14	11.10	
4 hr	165	0.590	6.60	6.61	
	140	0.905	5.05	8.93	10.27
	65	1.914	4.46	10.23	
	36	2.314	4.16	11.04	
6 hr	165	0.562	7.42	5.78	
	140	0.924	4.96	9.11	10.00
	65	2.001	4.51	10.11	
	36	2.352	4.07	11.30	
8 hr	165	0.538	7.03	6.15	
	140	0.876	4.85	9.33	10.81
	65	1.871	4.28	10.70	
	36	2.333	4.20	10.93	

Appendix C-2

Experimental Data & Results for Printing Strength at 510nm of Barium Lithol Red in Joncryl 67 printed on duPont Tyvek

Milling Time	Anilox Roller#	Pigment Weight (g/m^2)	R (%)	K/S	k/S_p
10 min	165	0.548	14.37	2.55	
	140	0.878	8.83	4.71	5.01
	65	1.752	5.76	7.71	
	36	2.003	5.11	8.81	
30 min	165	0.567	11.80	3.30	
	140	0.933	7.72	5.52	5.78
	65	1.732	4.80	9.44	
	36	2.413	4.16	11.04	
1 hr	165	0.538	11.30	3.48	
	140	0.819	8.02	5.27	6.44
	65	1.806	4.77	9.51	
	36	2.398	4.46	10.23	
2 hr	165	0.582	10.52	3.81	
	140	0.947	7.18	6.00	6.45
	65	1.860	4.65	9.78	
	36	2.413	4.34	10.54	
4 hr	165	0.528	10.34	3.89	
	140	0.987	6.57	6.64	7.00
	65	1.880	4.68	9.71	
	36	2.590	4.25	10.79	
6 hr	165	0.572	9.14	4.52	
	140	0.883	6.48	6.75	7.69
	65	1.949	4.56	9.99	
	36	2.497	4.22	10.87	
8 hr	165	0.587	9.27	4.44	
	140	0.888	6.30	6.97	7.90
	65	1.875	4.65	9.78	
	36	2.408	4.34	10.54	

Appendix C-3

Experimental Data & Results for Printing Strength at 560nm of Phthalocyanine Blue in Joncryl 67 printed on duPont Tyvek

Milling Time	Anilox Roller#	Pigment Weight (g/m^2)	R (%)	K/S	k/S_p
10 min	165	0.495	16.63	2.09	
	140	0.710	12.80	2.97	4.22
	65	1.614	6.48	6.75	
	36	1.886	5.80	7.65	
30 min	165	0.595	10.96	3.62	
	140	0.905	7.53	5.68	6.12
	65	1.805	4.06	11.34	
	36	2.048	3.99	11.55	
1 hr	165	0.619	8.73	4.77	
	140	0.929	6.10	7.23	7.68
	65	1.776	3.74	12.39	
	36	2.076	3.65	12.72	
2 hr	165	0.633	8.03	5.27	
	140	0.971	5.02	8.99	8.75
	65	1.857	4.03	11.43	
	36	2.076	3.65	12.72	
4 hr	165	0.619	7.70	5.53	
	140	0.981	5.69	7.82	8.30
	65	1.871	3.64	12.75	
	36	2.276	3.57	13.02	
6 hr	165	0.586	7.75	5.49	
	140	0.976	5.03	8.97	9.22
	65	1.943	3.77	12.28	
	36	2.252	3.60	12.91	
8 hr	165	0.624	7.43	5.77	
	140	0.981	4.90	9.23	9.33
	65	2.081	4.11	11.19	
	36	2.286	3.77	12.28	

Appendix D-1

Experimental Data & Results for Printing strength at 400nm of Diarylide Yellow in Joncryl 67 printed on Finch Offset

Milling Time	Anilox Roller#	Pigment Weight (g/m^2)	R (%)	K/S	k/S_p
10 min	200	0.190	29.05	0.87	
	165	0.471	13.00	2.91	
	140	0.810	7.08	6.10	7.53
	65	1.719	4.27	10.73	
30 min	200	0.190	28.19	0.91	
	165	0.448	11.92	3.25	
	140	0.848	6.18	7.12	8.40
	65	1.738	3.80	12.18	
1 hr	200	0.238	25.78	1.07	
	165	0.562	9.22	4.47	
	140	0.895	5.26	8.53	9.53
	65	1.752	3.75	12.35	
2 hr	200	0.219	24.78	1.17	
	165	0.510	9.18	4.49	
	140	0.848	5.22	8.60	10.14
	65	1.786	3.75	12.35	
4 hr	200	0.200	21.73	1.41	
	165	0.533	9.04	4.58	
	140	0.905	4.49	10.16	11.23
	65	1.748	3.76	12.32	
6 hr	200	0.200	21.85	1.41	
	165	0.538	8.50	4.92	
	140	0.881	4.53	10.16	11.42
	65	1.971	3.79	12.21	
8 hr	200	0.248	21.76	1.41	
	165	0.510	8.67	4.81	
	140	0.929	4.27	10.73	11.55
	65	1.933	3.84	12.04	

Appendix D-2

Experimental Data & Results for Printing Strength at 510nm of Barium Lithol Red in Joncryl 67 printed on Finch Offset

Milling Time	Anilox Roller#	Pigment Weight (g/m^2)	R (%)	K/S	k/S_p
10 min	200	0.188	36.74	0.54	
	165	0.503	17.36	1.97	
	140	0.839	8.22	5.12	6.10
	65	1.692	4.43	10.31	
30 min	200	0.173	35.65	0.58	
	165	0.528	14.26	2.58	
	140	0.868	7.38	5.81	6.69
	65	1.811	4.26	10.76	
1 hr	200	0.247	34.21	0.63	
	165	0.538	12.97	2.92	
	140	0.962	6.28	7.00	7.28
	65	1.826	4.21	10.90	
2 hr	200	0.192	31.49	0.75	
	165	0.563	10.94	3.63	
	140	0.957	5.99	7.38	7.71
	65	1.860	4.19	10.95	
4 hr	200	0.276	26.21	1.04	
	165	0.597	11.47	3.42	
	140	0.957	5.60	7.96	8.32
	65	2.023	4.21	10.90	
6 hr	200	0.222	30.37	0.80	
	165	0.528	11.77	3.31	
	140	0.952	5.47	8.17	8.58
	65	1.993	4.33	10.57	
8 hr	200	0.222	27.45	0.96	
	165	0.671	9.94	4.08	
	140	1.056	5.42	8.25	7.81
	65	2.161	4.41	10.36	

Appendix D-3

Experimental Data & Results for Printing Strength at 560nm of Phthalocyanine Blue in Joncryl 67 printed on Finch Offset

Milling Time	Anilox Roller#	Pigment Weight (g/m^2)	R (%)	K/S	k/S_p
10 min	200	0.119	55.36	0.18	
	165	0.348	33.37	0.67	
	140	0.590	23.24	1.27	2.15
	65	1.419	12.88	2.95	
30 min	200	0.133	35.63	0.58	
	165	0.405	22.23	1.36	
	140	0.743	12.09	3.20	4.28
	65	1.629	6.13	7.19	
1 hr	200	0.157	34.64	0.62	
	165	0.452	16.41	2.13	
	140	0.814	8.52	4.91	6.03
	65	1.619	5.19	8.66	
2 hr	200	0.190	30.69	0.78	
	165	0.552	12.41	3.09	
	140	0.838	7.28	5.90	7.04
	65	1.762	3.66	12.68	
4 hr	200	0.205	30.79	0.78	
	165	0.533	11.81	3.29	
	140	0.862	5.69	7.82	9.07
	65	1.810	3.71	12.50	
6 hr	200	0.238	28.75	0.88	
	165	0.562	10.62	3.76	
	140	0.886	5.24	8.57	9.67
	65	1.843	3.50	13.30	

Appendix E

Experimental Data & Results for Printing Strength at 400 nm of Diarylide Yellow in Joncryl 67 printed on Mead Offset

Milling Time	Anilox Roller#	Pigment Weight (g/m^2)	R (%)	K/S
8 hr	165	0.652	3.63	12.79
	140	0.862	3.58	12.98
	65	1.429	3.72	12.46
	36	1.467	3.75	12.35

Appendix F-1

Experimental Data & Results for Tinting Stregth at 440nm of Diarylide Yellow in Joncryl 678

Milling Time	Pig. Conc. (%)	R_m (%)	R_t (%)	K/S	k/s
10 min	0.93	43.05	63.45	0.105	
	1.86	33.68	53.22	0.206	
	4.68	22.59	38.14	0.502	
	9.79	15.18	25.61	1.080	10.9
30 min	1.18	37.32	57.43	0.158	
	1.90	30.54	49.32	0.260	
	4.82	20.46	34.77	0.612	
	9.91	13.57	22.56	1.329	13.1
1 hr	1.09	36.01	55.95	0.173	
	1.90	29.08	47.42	0.292	
	5.04	18.76	31.95	0.725	
	10.20	12.65	20.75	1.513	14.8
2 hr	1.33	34.06	53.67	0.200	
	2.12	26.38	43.72	0.362	
	4.81	17.63	30.01	0.816	
	9.99	11.91	19.27	1.691	16.8
4 hr	1.14	32.15	51.35	0.230	
	2.36	23.33	39.21	0.471	
	4.61	17.01	28.92	0.874	
	10.74	10.70	16.78	2.064	19.2
6 hr	1.06	32.53	51.82	0.224	
	2.01	24.37	40.82	0.429	
	5.31	15.10	25.46	1.091	
	9.95	10.77	16.92	2.040	20.5
8 hr	1.04	32.12	51.32	0.231	
	1.90	24.55	41.09	0.422	
	4.80	15.48	26.16	1.042	
	10.52	10.08	15.46	1.311	21.7

Appendix F-2

Experimental Data & Results for Tinting Strength at 440nm of Diarylide Yellow in Cropolamid 18W26

Milling Time	Pig. Conc. (%)	R_m (%)	R_t (%)	K/S	k/s
10 min	0.92	46.46	66.73	0.083	
	1.60	39.04	59.31	0.140	
	5.12	23.80	39.98	0.451	
	9.78	16.40	27.84	0.935	9.7
30 min	1.44	37.35	57.46	0.157	
	2.08	32.64	51.96	0.222	
	4.84	22.31	37.71	0.514	
	9.74	14.73	24.77	1.142	11.3
1 hr	1.43	35.53	55.40	0.180	
	1.99	31.01	49.92	0.251	
	4.43	21.74	36.82	0.542	
	9.80	13.75	22.91	1.297	12.9
2 hr	1.32	35.80	55.71	0.176	
	2.76	26.13	43.37	0.370	
	4.99	19.31	32.88	0.685	
	9.98	12.98	21.41	1.442	14.0
4 hr	1.59	32.29	51.53	0.228	
	2.10	28.78	47.02	0.298	
	4.64	19.23	32.74	0.691	
	9.68	12.72	20.89	1.498	15.0
6 hr	1.26	34.64	54.36	0.192	
	1.84	29.47	47.93	0.283	
	4.86	18.42	31.38	0.750	
	9.24	13.03	21.50	0.143	15.4
8 hr	1.14	35.15	54.96	0.185	
	2.72	24.07	40.38	0.440	
	5.02	17.51	29.80	0.827	
	10.07	11.81	19.07	1.717	16.6

Appendix F-3

Expermental Data & Results for Tinting Stregth at 440nm of Diarylide Yellow in Cropolamid 18W58

Milling Time	Pig. Conc. (%)	R_m (%)	R_t (%)	K/S	k/s
10 min	1.17	42.78	63.18	0.107	
	2.26	33.85	53.42	0.203	
	4.83	23.96	40.22	0.444	
	10.26	15.80	26.75	1.003	9.5
30 min	1.64	35.00	54.78	0.187	
	2.45	29.56	48.05	0.281	
	5.20	21.05	35.72	0.578	
	10.10	14.22	23.81	1.219	11.6
1 hr	1.23	38.50	58.72	0.145	
	2.19	31.02	49.93	0.251	
	4.44	22.43	37.89	0.509	
	10.19	14.10	23.58	1.238	11.8
2 hr	1.34	36.21	56.18	0.171	
	2.23	29.76	48.31	0.277	
	5.37	19.68	33.49	0.660	
	10.38	13.39	22.21	1.362	12.8
4 hr	1.32	34.12	53.75	1.990	
	2.29	27.32	45.04	0.335	
	4.83	18.80	32.02	0.722	
	9.84	12.72	20.89	1.498	15.1
6 hr	1.11	36.00	55.94	0.174	
	2.32	26.70	44.17	0.353	
	5.38	17.60	29.96	0.819	
	9.86	12.33	20.11	1.587	15.6
8 hr	1.51	31.45	50.48	0.243	
	2.41	25.55	42.54	0.388	
	4.53	18.77	31.97	0.724	
	9.92	12.04	19.53	1.658	16.4

Appendix G-1

Experimental Data & Results for Printing Strength at 400nm of Diarylide Yellow in Joncryl 678 printed on Finch Offset

Milling Time	Anilox Roller#	Pigment Weight (g/m^2)	R (%)	K/S	k/S_p
10 min	200	0.166	30.12	0.81	
	165	0.395	15.47	2.31	
	140	0.729	8.49	4.93	6.76
	65	1.624	4.75	9.55	
30 min	200	0.190	30.30	0.80	
	165	0.467	13.20	2.85	
	140	0.710	7.90	5.37	7.56
	65	1.500	4.41	10.36	
1 hr	200	0.186	27.50	0.96	
	165	0.476	12.16	3.17	
	140	0.767	6.13	7.19	9.37
	65	1.638	3.98	11.58	
2 hr	200	0.214	24.57	1.16	
	165	0.505	10.78	3.69	
	140	0.705	6.53	6.69	9.49
	65	1.695	3.87	11.94	
4 hr	200	0.214	24.26	1.18	
	165	0.448	10.61	3.77	
	140	0.748	5.51	8.10	10.83
	65	1.738	4.10	11.22	
6 hr	200	0.224	22.97	1.29	
	165	0.467	11.99	3.23	
	140	0.738	5.11	8.81	11.94
	65	1.719	4.05	11.37	
8 hr	200	0.200	23.75	1.22	
	165	0.510	9.33	4.41	
	140	0.838	4.81	9.42	11.24
	65	1.890	4.10	11.22	

Appendix G-2

Experimental Data & Results for Printing Strength at 400nm of Diarylide Yellow in Cropolamid 18W26 printed on Finch Offset

Milling Time	Anilox Roller#	Pigment Weight (g/m^2)	R (%)	K/S	k/S_p
10 min	200	0.163	32.48	0.70	
	165	0.408	16.47	2.12	
	140	0.700	10.28	3.92	5.60
	65	1.616	4.62	9.85	
30 min	200	0.181	29.49	0.84	
	165	0.478	15.17	2.37	
	140	0.881	7.02	6.16	6.99
	65	1.686	3.87	11.94	
1 hr	200	0.228	26.47	1.02	
	165	0.508	13.62	2.74	
	140	0.834	7.34	5.77	6.92
	65	1.832	3.61	12.87	
2 hr	200	0.204	25.72	1.07	
	165	0.525	12.29	3.13	
	140	0.887	6.36	6.89	7.77
	65	1.785	3.93	11.74	
4 hr	200	0.181	26.77	1.00	
	165	0.513	12.09	3.20	
	140	0.858	5.96	7.42	8.65
	65	1.878	3.66	12.68	
6 hr	200	0.187	26.16	1.04	
	165	0.438	12.64	3.02	
	140	0.776	6.10	7.23	9.32
	65	1.727	3.75	12.35	
8 hr	200	0.222	22.70	1.32	
	165	0.449	12.18	3.17	
	140	0.840	5.56	8.02	9.55
	65	1.943	3.87	11.94	

Appendix G-3

Experimental Data & results for Printing Strength at 400nm of Diarylide Yellow in Cropolamid 18W59 printed on Finch Offset

Milling Time	Anilox Roller#	Pigment Weight (g/m^2)	R (%)	K/S	k/S_p
10 min	200	0.140	44.26	0.35	
	165	0.350	26.70	1.01	
	140	0.675	13.39	2.80	4.15
	65	1.700	4.20	10.93	
30 min	200	0.146	41.28	0.42	
	165	0.426	23.40	1.25	
	140	0.764	10.26	3.92	5.13
	65	1.871	3.61	12.87	
1 hr	200	0.159	41.00	0.42	
	165	0.414	20.46	1.55	
	140	0.764	10.08	4.01	5.25
	65	1.922	3.26	14.35	
2 hr	200	0.159	39.98	0.45	
	165	0.445	19.89	1.61	
	140	0.821	9.32	4.41	5.37
	65	1.985	3.67	12.64	
4 hr	200	0.172	37.72	0.51	
	165	0.477	18.37	1.81	
	140	0.751	9.14	4.52	6.02
	65	1.775	3.61	12.87	
6 hr	200	0.178	35.41	0.59	
	165	0.382	17.79	1.90	
	140	0.738	8.39	5.00	6.78
	65	1.903	3.56	13.06	
8 hr	200	0.165	35.93	0.57	
	165	0.484	16.18	2.17	
	140	0.764	7.94	5.34	6.99
	65	1.826	3.47	13.43	

VITA

Junichi Tatsumi was born on April 1, 1951, in Nara, Japan, the son of Mitsuo and Teruko Tatsumi. He attended Kudan High School in Tokyo and he entered Kwansei-Gakuin University in Hyogo in April, 1969. He was graduated with Bachelor of Science degree in chemistry in March, 1973, after which he worked as a research chemist for Arakawa Chemical Industries, Ltd. in Osaka, Japan. He was selected a foreign student of his company in 1977 and entered the Graduate School at Lehigh University in August, 1978.